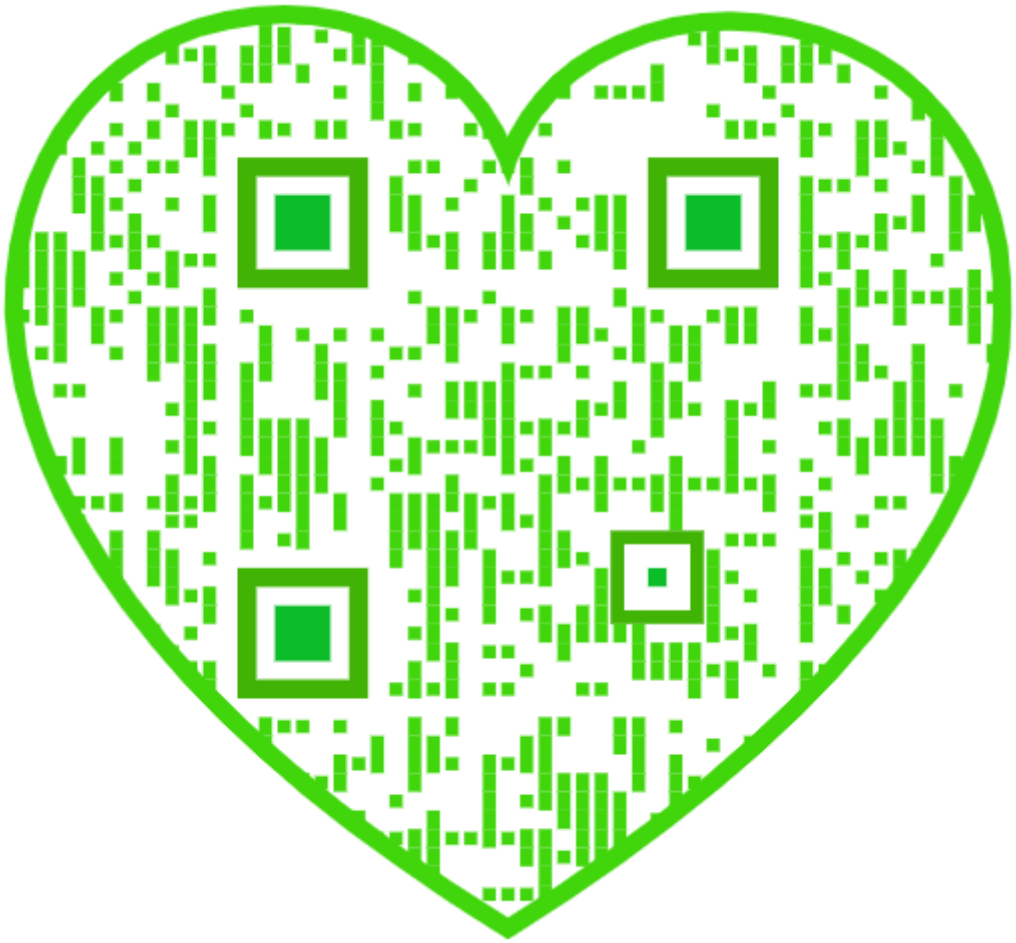

A TEXT-BOOK OF CHEMISTRY

JONES

A

TEXT-BOOK OF CHEMISTRY

FOR THE USE OF

STUDENTS AND PRACTITIONERS OF MEDICINE, DENTISTRY AND PHARMACY

BY

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TO THE MEMORY OF MY GRANDFATHER

DOCTOR JAMES LAWRENCE JONES

WHOSE EXEMPLARY CHARACTER AND ENNOBLING PRECEPT, WHOSE SCHOLARLY ATTAINMENTS AND SKILL AS A PHYSICIAN, HAVE EVER BEEN SOURCES OF INSPIRATION TO THE AUTHOR

THIS VOLUME IS

RESPECTFULLY AND AFFECTIONATELY INSCRIBED

PREFACE.

In this volume the author has endeavored to include all that is needed in chemistry for students of medicine, dentistry and pharmacy, and, at the same time, care has been exercised to avoid the introduction of unnecessary material.

The text is based upon a system of teaching which has been successfully followed for nine years; and the subject is presented in an inductive manner, commencing with simple statements and avoiding technical terms, until the student has begun to acquire familiarity with his work.

The atomic weights used are those adopted in the United States Pharmacopoeia, Eighth Decennial Revision, taken from the report of the International Committee on Atomic Weights for 1904, and are given in a table in the body of the book. In the description of each element the atomic weight is given in the nearest approximate whole number to that expressed in the table.

The references to the United States Pharmacopoeia are based upon the eighth decennial revision, to which this book is made to conform in regard to official preparations and chemicals. The expressions of specific gravity and solubility are based upon the new standard of temperature, as adopted by the Pharmacopoeia, viz., 25° C., 77° F. All statements of temperature, unless otherwise specified, are given in terms of the centigrade scale.

The author has not seen fit to depart from the present system of orthography by the introduction of such words as chlorin, bromin, sulfid, morphin, glucosid, etc., believing that such a system, if rigidly applied, would lead to the formation

of undesirable terms, and would interfere with the classification of many active medicinal agents, such as the alkaloids and glucosides.

The writer is indebted for material to many authors, and especially to the following: Bartley, Remsen, Simon, Ogden, Vaughan and Novy, Rockwood, Bunge, Brubaker and Heitzmann.

The drawings for illustrations were furnished by Dr. John W. Broadnax and the section on urinary concretions and sediments was furnished by Dr. E. G. Hopkins; to both of these gentlemen the author wishes to express his most grateful thanks.

JUNE 30, 1905.

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A TEXT-BOOK OF CHEMISTRY.

INTRODUCTION.

Chemistry has for its object a study of the essential nature and properties of matter, the changes of constitution which matter undergoes, and the laws relating to these changes. It is concerned with modifications in structure, and changes occurring in constitution, whether by union or separation, of the various forms of matter; and it also includes an investigation of the rules, or laws, which are constantly in action to produce these changes. In studying the essential nature of matter, chemistry furnishes the method of inquiry in relation to its composition, its internal structure, and its ultimate character. Chemistry also considers *the properties of matter, or its peculiar qualities,* by which we may recognize its different forms, and its suitability for utilization in different ways.

This science finds abundant application in the art of medicine and the associated professions of pharmacy and dentistry; it furnishes the methods for obtaining the medicinal agents which are used in the treatment of disease, and the substances which are employed for the preservation of health; it gives information in reference to the substances used as articles of food, and a warning and means of protection against those which act as poisons; it gives information in regard to the composition of the body, and in reference to changes taking place in the tissues; and it affords a means by which we may recognize the presence of disease.

A branch of science which is directed to the study of matter, or the material substance of which the universe is composed,

may seem too extensive for inclusion in one department of human knowledge, but a close investigation of the great number of bodies presented to our senses will reveal the fact that they are made up of a comparatively small number of simple or elementary substances. These simple, elementary forms of matter, by their existence in various modifications and combinations, produce the endless array of materials with which we are familiar.

The changes which are constantly taking place in nature, such as the disintegration of rocks or the evaporation of water, are known as *phenomena,* and a study of these changes will clearly show that they consist of two kinds, viz: Those which result in an entire change in the nature of substances, such as are produced by combustion; and those which are of a temporary or less serious character, such as the formation of ice. These two classes of phenomena are studied in the sciences of chemistry and physics, but since the phenomena are so closely associated in nature the sciences are incapable of complete separation. It is for these reasons that the subject of physics will be given a brief consideration after we have directed our attention in a general way to a study of the properties of matter.

PROPERTIES OF MATTER.

Matter is anything that occupies space, and that is revealed to our senses by its properties. For convenience of study, the properties of matter may be divided into two classes. This division embraces a consideration of the General Properties of matter, on the one hand, and the Specific Properties of matter, on the other.

GENERAL PROPERTIES OF MATTER.

The general properties of matter are those properties which pertain to all forms of matter. They are, extension, divisibility, compressibility, porosity, inertia and indestructibility.

Extension, or Figure, is a term used to express the fact that all matter occupies space; that is, it has length, breadth and thickness. This being true, every piece of matter has its boundaries, and the quantity of matter residing within these boundaries is called *mass.*

Divisibility is the property in virtue of which matter is capable of being divided. A substance may be ground to a powder so fine that the particles are invisible to the unaided eye, but these particles, when viewed under the microscope, will appear large and irregular. Further subdivision may be accomplished by dissolving the substance in a liquid—a grain of strychnine will impart a bitter taste to a barrel of water, and the particles of strychnine which give rise to the bitter taste in a drop of this water must be of exceeding smallness. Subdivision even greater than this may be accomplished by chemical change, and further division may still occur as a result of the action of electrical energy in vacuum tubes, or in the emanations from radium. See radium, page 181.

Compressibility is the property by which matter may be caused to occupy less space. If we apply pressure to a gas, the volume will be thereby lessened; and, in like manner, the volume of a liquid or solid may be reduced by pressure. Seeing that all matter is compressible, we have to conclude that it does not completely fill all the space within its boundaries.

Porosity is the property of having spaces or pores between the particles of which matter is composed. This property is at once suggested to the mind by the fact that all matter is compressible. These spaces can be clearly seen by the unaided eye in some substances of an extremely porous character, such as charcoal and cork: in other bodies they are in no wise visible, even with the aid of the most powerful microscope; yet we know that apparently dense substances are porous, for gases, and even liquids, may be forced through

them by means of powerful pressure. Thus it is that matter has an internal as well as an external surface. The internal surface is that surface which goes to make up the pores or spaces between the particles, while the external surface is that which bounds the mass.

Molecules. In assuming that matter is porous, and in assuming that spaces lie within its boundaries, we must at the same time assume that matter is composed of small particles, between and among which these spaces reside. In fact, it is impossible for us to conceive of the internal nature of matter in more than two ways, and these are, that matter is either homogeneous throughout and occupies all the space within its boundaries, or that it is made up of small particles and does not completely fill this space. The properties of porosity and compressibility point to the belief that matter is made up of small particles, and these small particles are called molecules. Molecules may be defined as the smallest particles of matter that have separate existence. The molecules of a body are not in absolute contact, and the spaces intervening between them are called intermolecular spaces. Furthermore, the molecules are known to be in a constant state of vibration.

All matter is found in one of three states of aggregation: it is found in the solid, the liquid, or the gaseous state.[1] Some substances occur only as solids; others occur as solids or liquids; and some can be obtained in the solid, liquid or gaseous state, under varying conditions.

In solid bodies, the molecules occupy fixed positions in relation to each other, and the form of the body cannot be changed without the application of force.

In liquids, the molecules are free to glide upon each other

[1] A fourth form of matter is believed to exist in the emanations from radium, and in the "cathode rays" of an electrical discharge through a vacuum tube. This is known as the ultra-gaseous or corpuscular form of matter, and is believed to consist of subdivided atoms.

and to change their relative positions, so that the body is mobile and accommodates its shape to that of the containing vessel.

In gases, the molecules not only glide upon each other but have a tendency to advance in straight lines, and thus tend to increase the volume of the body.

Inertia is the property of matter in virtue of which it cannot, of itself, change its condition. In whatever condition matter happens to be placed, it must remain in that condition until force be applied to produce a change.

Indestructibility. Matter cannot be destroyed. We may tear, rend or grind a substance, but we cannot lessen the quantity of matter which it represents. Fire is considered the most destructive of all agents, but it is not capable of destroying matter; for if we burn a substance, and examine the products of combustion we invariably find in them all the matter which was contained in the body burned. Matter may be changed but not destroyed.

SPECIFIC PROPERTIES OF MATTER.

Specific properties are the properties presented by certain definite bodies. We say of silver, a definite body, that it is a white, shining, malleable, ductile solid, all of which terms are expressive of specific properties. The specific properties worthy of special mention are, tenacity, ductility, malleability, hardness, transparency, translucency, opacity, color, odor and taste.

Tenacity. When a body shows great resistance to the separation of its parts it is said to be tenacious.

Ductility is the capability of changing form by action of traction or pressure. This property is exhibited in those bodies which may be drawn out in the form of wire, and it is highly developed in the metals, gold, silver and platinum.

Malleability is the property of being reducible to thin leaves by hammering or by passing between rollers. Gold is the most malleable of the metals, being reducible to 1/256,000th of an inch in thickness.

Hardness is the resistance which a substance opposes to being scratched or penetrated. The relative hardness of two bodies is determined by ascertaining which of the two will scratch the other.

Transparency is the property of allowing the free passage of light. Objects may be seen through transparent bodies.

Translucency is the property of allowing some light to pass through, but objects cannot be seen through translucent bodies.

Opacity. Opaque substances obstruct the passage of light to a greater or less degree.

PART I.

PHYSICS.

Before entering upon a detailed study of the chemical relations of matter it is desirable to give a brief sketch of certain branches of physical science, the study of which is necessary to an understanding of chemical methods and reactions.

Physics, as distinguished from chemistry, is chiefly concerned with the study of energy. The changes taking place in matter which do not affect its essential nature are physical changes, and a study of the forms of energy producing these changes is embraced in the science of physics.

ENERGY.

Energy is made manifest to the senses by the effect it produces upon matter;—as the falling of a body to the earth, or heating a platinum wire by the passage of an electrical current. With the expenditure of energy a corresponding change is produced upon matter, and the production of this change is called *work.*

Potential Energy is energy stored up. A stone held some distance from the surface of the earth contains potential energy on account of its position, for when its support is removed the stone falls to the earth, thus making the energy manifest. A wound watch spring contains potential energy, on account of its condition of tension.

Kinetic Energy is energy in action, and is seen in the falling stone, or in the rapidly unwinding watch spring.

The forms of energy of interest to the student of chemistry are *cohesion, adhesion, gravitation, heat, light and electricity.*

Cohesion is the force of attraction exerted between similar kinds of molecules, and holds the particles of matter together in the form of mass. Cohesion is very strongly exerted between the molecules of solid bodies, and causes their mass to preserve a definite form. In the case of liquids cohesion is more feebly exerted, and in gases it seems to be suspended.

Adhesion, or Surface Action is the attraction exerted between the molecules upon the surfaces of bodies in contact. This form of attraction takes place between the molecules upon the external surfaces of bodies, as shown by pressing two plates of glass firmly together, when they will adhere, or stick; it also takes place between the molecules upon the internal surfaces of bodies, as shown by dissolving solid bodies in liquids, or by the absorption of gases by charcoal.

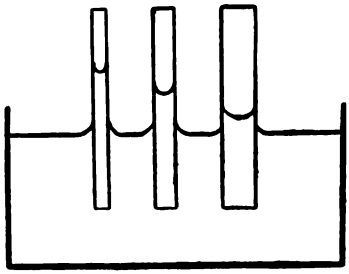
Most solid bodies when dipped into a vessel of water are made wet, and this wetting is due to the fact that adhesion between the molecules of the solid and the liquid is sufficiently strong to overcome the force of cohesion between the molecules of water. In some instances a liquid does not wet a solid, as is seen in the case of a glass rod dipped into a vessel of mercury: in this case the force of adhesion is too feeble to overcome cohesion.

The surface of a liquid contained in a narrow vessel always shows a concave appearance when adhesion is exerted between the liquid and the sides of the container. It is for this reason that the surface of water contained in a small glass tube presents a higher level at its circumference than at its center. The curved surface so formed is called a *meniscus,* and, in reading the level of the liquid in measuring, either the center or circumference of the curved surface has to be selected. A further manifestation of adhesion is shown when capillary

glass tubes are dipped into a vessel of water: in this case the level of the water in the tubes will be higher than the level of the water on the outside. This action is known as *capillary attraction.* The extent to which capillary attraction is exerted depends upon the nature of the liquid, the temperature, and the diameter of the tube; it is inversely proportional to the diameter of the tube, and it is lessened by the action of heat. Where a liquid does not wet a solid there is capillary depression instead of elevation, and the surface of the liquid is convex instead of concave.

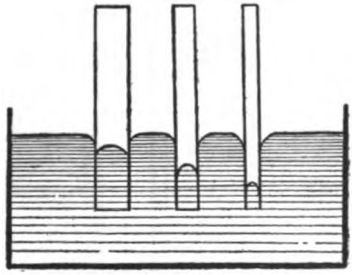
Adhesion between solids and gases is indicated by the fact that solid bodies weigh less when hot than when cold. Solids

FIG. 1.



Capillary Attraction.

FIG. 2.



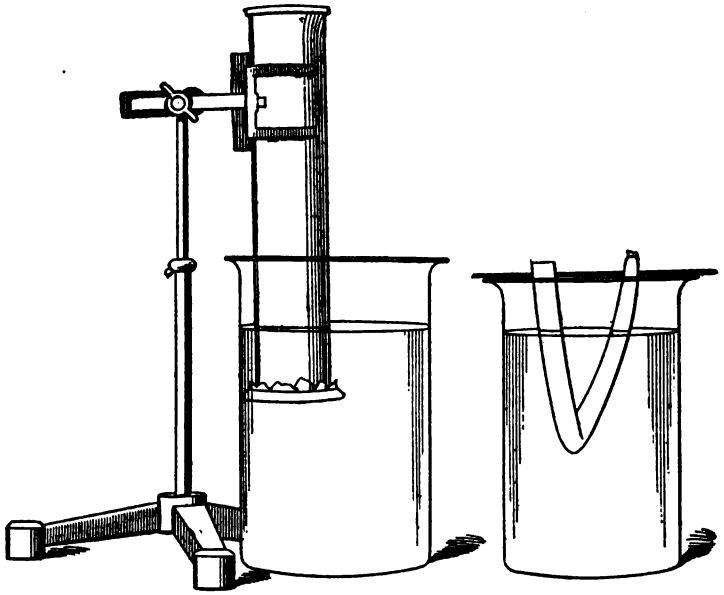
Capillary Depression.

have atmospheric gases adhering to the surface, which are driven off by heat. Adhesion between liquids and gases is indicated by the solution of gases in water. In some cases the solubility is very great. Solution is favored by the action of pressure and the abstraction of heat.

Diffusion means the intermingling or mixing of masses of gases or liquids by the motion of their molecules. This mixing may take place when the gases or liquids are placed in direct contact, or when a porous substance intervenes between them. If we place some water in the bottom of a test-tube and then

carefully pour a little alcohol upon its surface, in such manner that the alcohol and water form separate layers, and then allow the tube to stand for some time, it will be found that the alcohol and water gradually intermingle their particles and ultimately become thoroughly mixed. If a porous diaphragm of clay or animal membrane be interposed between the two liquids they will mix through the pores of these substances.

FIG. 3.



Dialyzer. (After Rockwood.)

Gaseous bodies brought together in the same way will thoroughly mix with each other. The rate of diffusion of gases through porous diaphragms takes place in a regular or uniform manner, and this fact is expressed in the law of Graham, which says: *The velocity of diffusion of a gas is inversely proportional to the square root of the density.* The

square root of the density of oxygen being four and that of hydrogen being one, the velocity of diffusion of hydrogen would be four times greater than that of oxygen.

Dialysis, or Osmosis. The investigations of Graham led to the discovery that certain solid bodies held in solution are capable of diffusing through porous membranes, such as parchment or bladder, while certain other bodies do not possess this property. The substances which thus diffuse are always crystallizable, while those which do not diffuse cannot be crystallized. He named the diffusible bodies, *crystalloids,* and the non-diffusible bodies, *colloids.* These phenomena are referred to in the terms, *dialysis, or osmosis,* and they are investigated by means of the *dialyzer.*

The dialyzer consists of a glass cylinder open at both ends, over one end of which is tied a membrane of parchment or bladder, which is placed in contact with water contained in another vessel of larger size. The liquid to be dialyzed is placed upon the porous membrane in the smaller vessel, and this, in turn, is placed upon water contained in the larger vessel. Solutions of crystalloids will pass from the inner vessel to the water in the outer vessel, and at the same time water passes in the opposite direction.

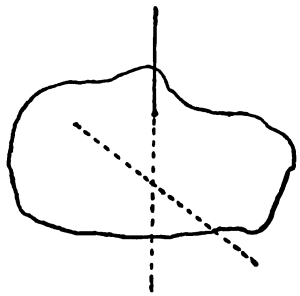
GRAVITATION.

Gravitation is the force of attraction exerted between masses of matter. It is a universal property of all masses of matter that they tend incessantly to approach each other, whether at rest or in motion; whether near together or separated by great distances. The force of gravitation holds the planetary bodies in position in the universe; it causes a stone to fall to the earth's surface. The force of attraction of gravitation between two bodies is directly proportional to the product of their masses, and inversely proportional to the square of the distance between them.

Terrestrial gravitation is shown in the tendency of bodies to fall to the earth's surface, and the direction taken by a falling body is called a *vertical line.* The vertical is determined by means of a plumb line, which consists of a weight tied to the end of a string and suspended by its free end. A line or plane drawn at right angles to the vertical is said to be *horizontal.* The surface of a liquid at rest always assumes the horizontal plane.

The center of gravity of a body is that point through which passes the resultant of the forces of attraction between the body and the earth. This point, in the case of a sphere of uniform density, is at its center; but, in the case of a body of irregular shape or of varying density, it may be found at a point some distance from the center, or even outside of the body. The center of gravity may be determined by suspending a body by means of a string in two different positions, and extending the line of suspension in each case; the point in the body at which the two lines intersect is the center of gravity.

FIG. 4.



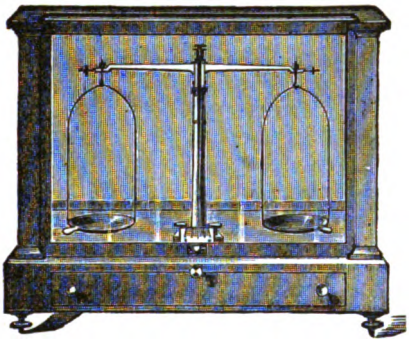
Method of Finding Center of Gravity.

Weight is an expression denoting the amount of attraction of the earth for the body weighed, as compared to that of a standard. It leaves out of consideration the attraction of the substance for the earth, which is so infinitely small that it can be disregarded.

The balance is the instrument generally employed for measuring weight. The instrument in its simplest form consists of a beam suspended at a point directly over the center of gravity

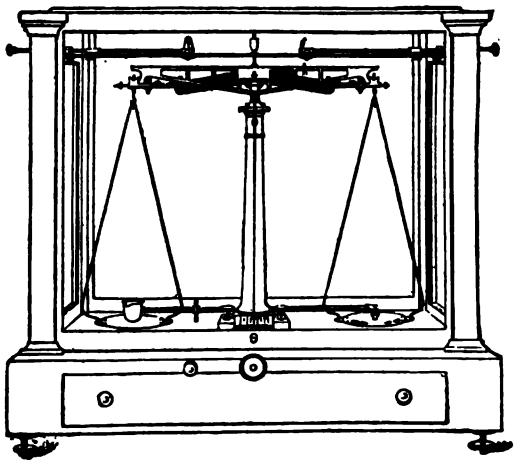
so that in oscillating it tends to assume a horizontal position. From a point near each extremity of this beam a scale pan is

FIG. 5.



Balance. (After Coblentz.)

FIG. 6.



Balance. (After Coblentz.)

suspended, in one of which the standard weight is placed and in the other the substance to be weighed. The axes of suspension of the balance consist of prisms whose sharp edges rest

upon supports of agate, in order to reduce the amount of friction to a minimum degree.

Systems of Weights and Measures. The standards for weighing and measuring at present in use in this country are the English, and the French, or Decimal.

The English System of Weights and Measures consists of:

Apothecaries' Weight.

20 Grains (gr.)	=	1 Scruple.
3 Scruples (℈)	=	1 Drachm.
8 Drachms (ʒ)	=	1 Ounce.
12 Ounces (℥)	=	1 Pound (℔).

Wine, or Fluid Measure.

60 Minims (Min.)	=	1 Fluid Drachm.
8 Fluid Drachms (fʒ)	=	1 Fluid Ounce.
16 Fluid Ounces (f℥)	=	1 Pint.
8 Pints (O)	=	1 Gallon (Cong.)

Measures of Length.

12 Inches (in.)	=	1 Foot.
3 Feet (ft.)	=	1 Yard (yd.)

The Imperial Gallon of the British Pharmacopœia contains 160 fluid ounces, 277.274 cubic inches, or 70,000 grains. The Imperial Pint contains 20 fluid ounces, 34.659 cubic inches, or 8,750 grains. Corresponding measures of the United States Pharmacopœia are somewhat different from these standards; the gallon containing 231 cubic inches, 128 fluid ounces, or 58,372.2 grains; and the pint containing 16 fluid ounces, 28.875 cubic inches, or 7,296.525 grains.

The French, Metric, or Decimal System of Weights and Measures. The unit of this system is the Meter, which is the length of a platinum bar kept in the public archives of France. The length of this bar is equal to one forty-millionth part of the circumference of the earth through the poles.

The Meter is employed as the unit for measuring length, and its equivalent in the English system to 39.37 inches.

The Liter is the unit of capacity, and is employed for measuring volume. It is obtained by taking the cubic contents of one-tenth of the meter—a cubic decimeter—and contains one thousand cubic centimeters. Its equivalent in the English system is 33.81 fluid ounces.

The Gram is the unit of weight, and is obtained by taking the weight of a cubic centimeter of water at 4 degrees Centigrade, which is the temperature of greatest density of water. The equivalent of the gram in the English system is about 15.43 grains.

The ratio of increase and decrease of these several units is decimal, and for this reason the system is sometimes called the decimal system. Multiples of the units are indicated by using the Greek prefixes, Deka, ten; Hecto, one hundred; Kilo, one thousand. Sub-multiples are indicated by using the Latin prefixes, Deci, one-tenth; Centi, one-hundredth; Milli, one-thousandth.

Table of Metric Weights and Measures.

Kilo	———	———	———	1000.
Hecto	———	———	———	100.
Deka	———	———	———	10.
	Meter.	Liter.	Gram.	
Deci	———	———	———	1/10.
Centi	———	———	———	1/100.
Milli	———	———	———	1/1000.

DENSITY AND SPECIFIC GRAVITY.

The expression *density* is a term used to denote the mass or quantity of matter contained in a body compared with the quantity of matter contained in a standard body of equal volume. *Specific gravity* is a term used to express the relative weights of two bodies of equal volume, one of which is taken as the unit of comparison. Perfectly pure water, at the temperature of 25° C. or 77° F., U. S. P. 1900, is taken as the standard in expressing the specific gravity of solids and liquids:

in the case of gases, air is used as the standard. While air is used as the standard of comparison in speaking of the specific gravity of gases, their *density* is expressed in terms which refer to hydrogen. A gas is said to have *specific gravity* as referred to air, and *density* as referred to hydrogen.

The specific gravity of a body is expressed by using a number which shows how many times the weight of a given volume of water is contained in the weight of an equal volume of the substance. Such a number will be greater or less than unity, as the substance in question is heavier or lighter than water.

Methods of Determining Specific Gravity. In all determinations of specific gravity the essential problems to be solved consist in finding and weighing equal volumes of the substance, and of the standard body; the weight of the substance is then divided by the weight of equal volume of standard, and the quotient expresses the specific gravity.

In Liquids, the specific gravity is easily found because of the simplicity of the methods required to find and weigh equal volumes. The method here consists in selecting a glass flask with a narrow neck and accurately balancing it upon the scales with a counterpoise of equal weight. Distilled water at a temperature of 25° C. is poured into the vessel until it contains exactly 1000 grains, and a mark is made on the neck of the flask at the level of the liquid. When this is finished the vessel is emptied of water and dried, and the liquid whose specific gravity it is desired to find is poured into the vessel until its level reaches the mark on the neck. This is then placed upon the scales and weighed, the counterpoise being retained to balance the weight of the empty flask. The weight of this liquid, which corresponds in volume to 1000 grains of water, is divided by the weight of the water—1000 grains. The quotient expresses the specific gravity.

Example:

Required, to find the specific gravity of sulphuric acid.

Weight of an empty glass flask	100 grains.
Weight of flask filled with water	1,100 grains.
Weight of water	1,000 grains.
Weight of flask filled with sulphuric acid	1,940 grains.
Weight of flask	100 grains.
Weight of acid	1,840 grains.

1,840 ÷ 1,000 = 1.840, specific gravity of the acid.

In Solids, the determination of specific gravity involves the same principles as above, but the methods are different. The specific gravity bottle is filled with water and weighed; then the solid is weighed separately. These two weights are added together, and the sum denotes the weight of the bottle, the water, and the solid. The solid body is then placed in the flask of water, when it displaces a quantity of water equal to its own volume. The displaced water is allowed to run out, the whole is again weighed, and loss in weight will indicate the weight of the volume of water displaced by the solid. The weight of the solid body is then divided by the weight of an equal volume of water, so found, and the quotient expresses the specific gravity.

Example:

Weight of solid body	50 grains.
Weight of flask of water	200 grains.
Combined weight	250 grains.
Weight of flask and solid after water is displaced by latter	230 grains.
Weight of water displaced	20 grains.

50 ÷ 20 = 2.5, specific gravity of solid.

Other methods are based upon the *Theorem of Archimedes.* This theory states that a body when weighed in water loses a portion of its weight, and the loss represents the weight of an equal volume of water. To determine specific gravity by the

theorem of Archimedes the solid is first weighed in air, then it is suspended by a thread or hair and weighed in water. The difference between the two weights represents the weight of a volume of water equal to the volume of the solid. The weight in air, therefore, divided by the loss of weight in water will give the specific gravity.

If the body to be examined is lighter than water, it is first weighed in the air, then attached to a piece of metal heavy enough to sink it, and both are weighed. The two are then weighed in water, and the loss in weight represents the weight of water displaced by both. The piece of metal is then detached and weighed in air and again in water; the loss of weight indicates the weight of water displaced by the metal alone. The difference between the weight of water displaced by the two together and that displaced by the metal alone gives the weight of water displaced by the light body. The weight of the light body is then divided by the weight of water which it displaces, and the specific gravity is obtained.

Example:

Wax weighs in air	133.7 grains.
Attached to brass the two weigh	183.7 grains.
In water the two weigh	38.8 grains.
Weight of water equal to bulk of brass and wax.	144.9 grains.
Weight of brass in air	50.0 grains.
Weight of brass in water	44.4 grains.
Weight of water equal to volume of brass	5.6 grains.
Weight of water equal to bulk of brass and wax.	144.9 grains.
Weight of water equal to bulk of brass alone	5.6 grains.
Weight of water equal to volume of wax	139.3 grains.

$133.7 \div 139.3 = 0.9598$, specific gravity of wax.

In case the solid is soluble in water some other liquid of known specific gravity is used, and from the weight of this liquid displaced, the weight of an equal volume of water is

calculated. The liquids used are alcohol, oil of turpentine or others. For example: The substance is weighed in air, then in oil of turpentine; the loss in weight indicates the weight of an equal bulk of oil of turpentine. From this weight of oil of turpentine of known specific gravity, the weight of an equal volume of water is easily calculated, and the specific gravity is obtained.

Example:

Weight of sugar in air..... 400 grains.
Weight of sugar in oil of turpentine..... 182.5 grains.
Weight of equal bulk of oil of turpentine.. 217.5 grains.

Assume the specific gravity of oil of turpentine to be 0.87: then,

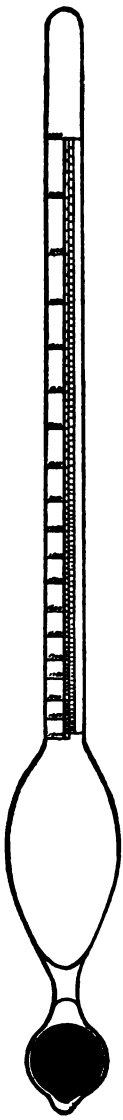
$0.87 : 100 :: 217.5 : x = 250$, weight of equal bulk of water.

Hence:

$400 \div 250 = 1.6$, specific gravity of sugar.

Hydrometers are instruments used to determine the specific gravity of liquids. They usually consist of a glass tube, the lower extremity of which is expanded and weighted so as to hold the instrument in a vertical position. The principle upon which their action depends is the fact that a solid body floating in a liquid heavier than itself displaces a volume of liquid equal to its own weight, and for this reason the hydrometer will sink deeper in light liquids than in heavy ones. By previously testing the instrument in liquids of known specific gravity and making a corresponding scale on the stem, the specific gravity of a liquid in which it may be immersed can be easily read off. These instruments, when made for the purpose of testing special liquids, are called urinometers, alcoholometers, lactometers, etc.

FIG. 7.



Hydrometer.

The specific gravity of a gas is determined by finding and weighing an equal volume of gas and of the standard, air, *under the same conditions of temperature and pressure.* The weight of the gas is then divided by the weight of an equal volume of air.

PHYSICAL CONSTITUTION OF GASES.

In considering the law of the attraction of masses of matter, or gravitation, the question naturally arises, Do gases have weight? The question can be very easily answered by a simple experiment. If a glass globe filled with air, and fitted with an air-tight stop-cock, be carefully weighed and then the air completely exhausted by means of the air-pump, it will be found that the vessel is considerably lighter upon re-weighing. This loss in weight must represent the weight of the air which the globe contained. If the vessel be of sufficient size to contain 100 cubic inches the loss in weight will amount to nearly 30 grains. This weight is made manifest in the enormous force with which the air presses down upon the earth's surface, but the pressure is so evenly distributed, on account of perfect mobility of the particles of air, that it causes no disagreeable effects. Any sudden and great change in atmospheric pressure, however, results disastrously to the living animal.

All other gases possess the property of weight. Those that are dense will sink to the lower level, but those that are lighter than air will rise, being buoyed up by the surrounding medium; just as a light body will rise when set free below the surface of water.

The Barometer. If a glass tube, sealed at one end and having a cross section of one square inch, be completely exhausted of air and inserted into a vessel of mercury, the mercury will be seen to rise in the tube until it reaches a point thirty inches from the surface of the liquid in the vessel. This

column of mercury is forced up into the empty tube on account of the pressure of air on the surface of the liquid. The weight of such a column of mercury is found to be about fifteen pounds—14.7—and the cross section being equal to one square inch, the weight of the atmosphere is fifteen pounds to the square inch of surface—nearly a ton to the square foot of 144 square inches.

The expression, "atmospheres," in pressure, is used to designate the amount of pressure to the square inch of surface: ten atmospheres, indicating one hundred and fifty pounds to the square inch; two atmospheres, indicating thirty pounds; one atmosphere indicating fifteen pounds, etc.

The instrument represented in the above experiment, when made of proper size and graduated to a scale, is called a *Barometer,* and it is used to measure atmospheric pressure. Atmospheric pressure is not constant at any one place, varying with climatic changes; it also constantly lessens with increasing elevation above the sea level.

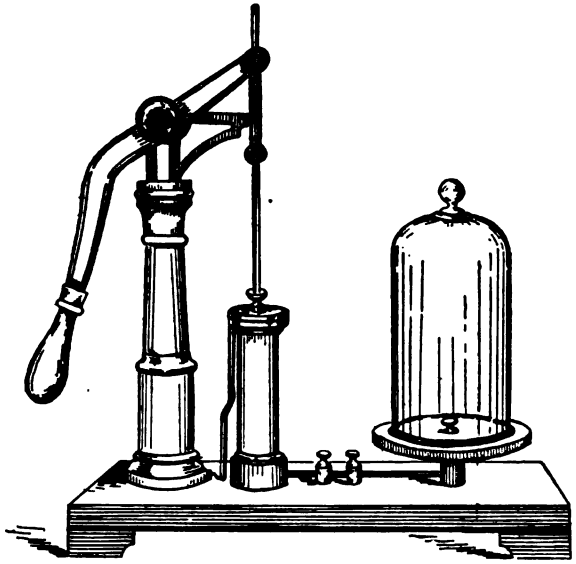
Other liquids than mercury may be used to construct a barometer, but as the height of the column is inversely proportional to the weight of the liquid used it would be much higher with lighter liquids. Water is 13.6 times lighter than mercury, and the height of the column would be 13.6 times 30, or about 34 feet.

The Air Pump is an instrument for producing a vacuum. The vessel in which the vacuum is produced, by exhaustion of air, is called the "receiver" of the air pump. This instrument consists of a hollow cylinder in which a tightly fitting piston is moved by its rod. The bottom of the cylinder communicates with the receiver of the pump, and contains a valve opening upward; a valve, opening in the same direction, is fitted in the piston. When the piston is raised, the lower valve opens and air is drawn into the cylinder from the receiver;

when the piston is depressed, the lower valve closes, the upper valve opens, and a cylinderful of air escapes to the surrounding atmosphere. Thus, a cylinderful of air is removed from the receiver at each stroke of the pump.

Sprengel's Air-Pump consists of a vertical glass tube the lower end of which dips into a vessel of mercury, the vessel being supplied with a spout just above the lower end of the

FIG. 8.



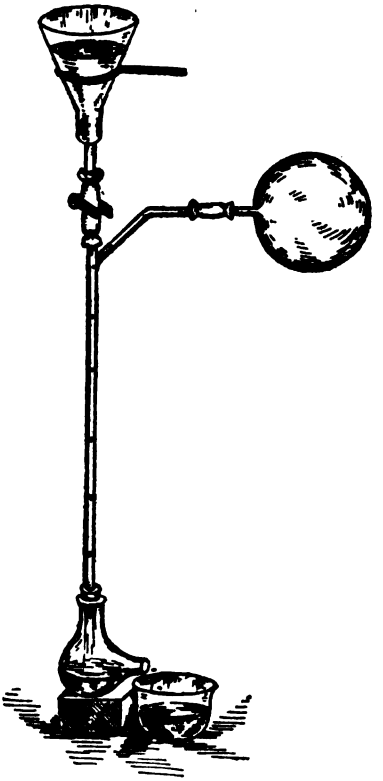
Air Pump.

tube to carry off excess of the liquid. The upper end of this tube is attached to a funnel by means of a piece of rubber tubing to which is fitted a clamp. From near the upper extremity of the vertical tube a lateral tube is extended, to the end of which is attached the vessel from which air is to be exhausted. To operate the instrument, mercury is poured into the funnel and allowed to flow through the vertical tube, the

flow being regulated by the clamp. As mercury passes down, air is carried with it, until complete exhaustion has occurred in the receiver, and the column stands at a height of 30 inches.

Elasticity, or Tension, is a property of gases in virtue of which they constantly tend to increase their volume. It is due to the fact that the molecules of a gas are constantly in motion, advancing in straight lines, and by continuously striking against the sides of the containing vessel produce the phenomenon of pressure. The volume, pressure, and elastic force of gases bear relations to each other which are expressed in the law discovered by Boyle in 1661, and generally known as *Boyle's law;* it is sometimes called Mariotte's law. The law may be expressed thus: *The volume of a gas is inversely as the pressure; the density and elastic force are directly as the pressure and inversely as the volume.* For example: If a vessel contains 100 cubic inches of a gas under a pressure of 10 pounds, the volume would be lessened to one-half, one-third, or one-fourth of 100 cubic inches if the pressure were increased to 20, 30 or 40 pounds. The density and elastic force would be *increased*

FIG. 9.



Sprengel's Air Pump.

to the same degree. All vapors, when not near the point of condensation, behave like gases in respect to this law.

HEAT.

The term, heat, is used to express a definite sensation, and also the condition of matter which produces this sensation.

Two theories have been advanced to explain the phenomena of heat. For a long time many philosophers believed heat to be a material substance, differing from other matter in lacking the property of weight, but existing in combination with other bodies, and capable of being transferred from one substance to another. The term *Caloric* was used to designate this hypothetical body.

At present, however, heat is believed to be a form of energy and not of matter. This theory was first advanced by Sir Humphrey Davy as a result of experiments showing that the quantity of heat produced by mechanical energy is directly proportional to the amount of energy expended, and not to the quantity of matter involved. It is called the *Dynamical, or Mechanical Theory,* and assumes that the phenomena of heat are caused by a vibratory or oscillatory motion of molecules and atoms. The vibratory motion is capable of being transferred from one substance to another, and the degree of heat bears a direct relation to the rapidity of vibrations.

PHYSICAL EFFECTS OF HEAT UPON MATTER.

Expansion.

One of the first and most visible effects of heat upon matter is a gradual increase in the volume of a heated body. Expansion as a result of heat occurs in solids, in liquids and in gases.

Expansion of Solids. If an iron bar be made to fit accurately to a gauge when cold, it will be found to have expanded

in all its dimensions when heated; and when allowed to cool down again, it will once more fit the gauge.

The degree of expansion for the same increment of heat is not alike for every solid substance, and the rate of expansion increases with increase of temperature. The force exerted in the expansion of solid bodies by heat is so great as to necessitate an allowance for change in volume of the component parts of structures of iron, or other metal, attendant upon changes of temperature.

Expansion of Liquids. The property of expansion by heat in liquids occurs to a greater extent than in solids, as may be shown by placing a liquid in a glass flask having a long narrow neck, and heating. Under these conditions, the level of the liquid in the neck of the flask will be seen to rise, indicating increase in volume on the part of the former, and showing, furthermore, that the rate of expansion of the contained liquid is greater than that of the container. With increase of heat the rate of expansion also increases, as in the case of solids. Mercury expands very regularly from 0° to 100° C.; and, for some distance above that point of temperature, expansion on the part of the glass container about equalizes the increased rate of expansion of the metal. Mercury expands about 1/64 of its volume from 0° to 100° C.

Water gives a very remarkable deviation from the law of expansion by heat, within certain limits of temperature. Throughout ordinary temperatures it behaves like other bodies. When cooled, it slowly contracts in volume until the temperature reaches 4° C. (39.2° F.), but below this point expansion begins, and continues as the temperature sinks, until the freezing point is reached at 0° C. In freezing, there is a sudden and great increase in volume. This unusual behavior on the part of water causes its coldest portions to rise to the surface, on account of their decrease in specific gravity, whenever the tem-

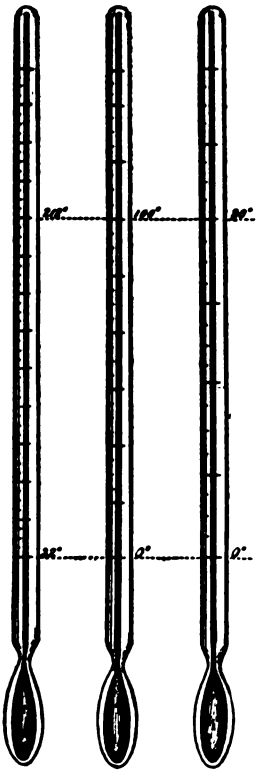
perature draws near the freezing point. These conditions are sufficient to account for the formation of ice upon the surface of bodies of water. The expansion of congelation at the moment of freezing is a phenomenon observed in many other bodies when they pass from the liquid to the solid state, and is of a different nature from that observed before the freezing point is reached. The force of the expansion of congelation is very great, and is sufficient to burst cast iron shells in which water has been placed and exposed to low temperatures. This force can be opposed by physical means, however, and to such an extent that the temperature of water can be carried far below the freezing point without congelation taking place. The expansion of congelation serves a very important function in nature. Water, accumulating in the crevices of rocks and soils, upon freezing, causes disintegration and exposure of soluble constituents, which are washed out by falling rains, and contribute to the sustenance of growing plants.

From what has been said in the above, it can be seen that the temperature of greatest density of water is that point at which contraction in volume with reduction of temperature ceases. This point of temperature is 4° C., or 39.2° F.

The Thermometer. The sensations are inaccurate when used for the purpose of measuring the degree of heat: a substance feels hot, or cold, in accord with a higher, or lower, temperature than that of the body. The instrument used for determining temperature is called a thermometer, and advantage is taken of the expansibility of matter by heat in selecting the material from which it is made. In constructing a thermometer, a glass tube is selected, having a capillary bore of uniform size and a bulb blown at one end. The bulb is heated to expel air, and the open end of the tube is dipped into a vessel of mercury. As a result of this, mercury rushes in the bulb by pressure of the atmosphere, partly filling the instru-

ment. If the bulb of the thermometer be now heated, so as to volatilize a portion of its contents, it may be completely filled by dipping the open end of the tube in the vessel of mercury. The instrument is now heated until sufficient mercury is expelled to allow the remainder to stand at a convenient height, and it is again heated until the contents completely fill the tube, when the latter is quickly sealed. When the mercury recedes a vacuum is left in the upper part of the instrument.

FIG. 10.



Thermometers, Showing the Three Different Scales.

The thermometer has now to be graduated by means of a scale, to which it is attached, or which is marked on the stem. This is done by placing it in melting ice for one of the fixed points of temperature, and then in steam rising from boiling water for the other. In the Centigrade scale, the freezing point is marked 0°, and the boiling point 100°; the intervening space being divided into 100 equal subdivisions. In the Fahrenheit scale, the freezing point is marked 32°, and the boiling point 212°; the intervening space being divided into 180 equal parts. In the Réaumur scale, the freezing and boiling points are marked 0° and 80°, respectively, with 80 equal divisions of the scale between these two points.

The divisions of the scale are also extended below the zero mark, and the readings here are indicated by the minus sign

(—). Readings above zero are expressed by using the plus sign (+).

The relation between the reading of the three scales is expressed by the figures which show the number of divisions between the freezing and boiling point for each scale: 80 for the Réaumur, 100 for the Centigrade, and 180 for the Fahrenheit. These numbers when reduced to their simplest terms are 4, 5, and 9, and they are used in converting the readings of one scale into those of the other. The Fahrenheit scale having been given 32 at zero, this number must be deducted when Fahrenheit degrees are calculated to the degrees of the other scales, and added, when Réaumur or Centigrade degrees are calculated to Fahrenheit.

To convert C. degrees to F. degrees; multiply by 9, divide the product by 5, and add 32.

Example: Convert 4 degrees C. to F. degrees:

$$5 : 9 :: 4 : x = 7.2 + 32 = 39.2 \text{ F.}$$

Example: Convert — 10 degrees C. to F. degrees:

$$5 : 9 :: -10 : x = -18 + 32 = +14 \text{ F.}$$

To convert F. degrees to C. degrees; subtract 32, multiply by 5, and divide the product by 9.

Example: Convert 60 degrees F. to C. degrees:

$$60 - 32 = 28.$$

$$9 : 5 :: 28 : x = 15.5 \text{ C.}$$

Example: Convert — 20 degrees F. to C. degrees:

$$-20 - 32 = -52.$$

$$9 : 5 :: -52 : x = -28.8 \text{ C.}$$

The spirit thermometer is intended for measuring unusually low temperatures, and is made by using colored alcohol instead of mercury for filling the bulb.

Expansion of Gases. When solids and liquids are heated the amount of expansion varies with different substances, but in the case of gases we find great uniformity in expansion. The amount of expansion for a given quantity of heat is alike for all gases, and this statement applies equally to vapors when the temperature is remote from the point at which they condense. The *Law of Charles* refers to the regularity with which gases expand under the influence of heat, and may be expressed thus: "With constant pressure, the volume of a gas increases regularly with increase of temperature, and decreases regularly with decrease of temperature." If the gas be confined and expansion prevented, the pressure will increase in proportion to the increase of temperature. The amount of expansion or contraction of a gas is 1/273, or .3665 per cent. of the volume at 0° C. for each degree of the same scale; and, therefore, 100 cubic inches of a gas at 0° C. would become 136.65 cubic inches at the temperature of 100° C.

Absolute Zero. If a gas contract 1/273 of its volume at zero for each degree of the same scale when cooled, it is clear, from a mathematical standpoint, that at 273° below zero it would be resolved to nothing. While this low temperature has never been reached in actual experiment, it is known that the gas would become a liquid, and then a solid, long before its temperature fell to this point. The point of temperature at which a gas shall have contracted in volume until it, theoretically, cease to exist, is called *absolute zero;* and here it is believed that all molecular motion is suspended, and that matter is devoid of heat. Absolute zero for the Centigrade thermometer is 273° below 0°; for the Fahrenheit it is 459° below. The absolute temperature of a substance may be found by adding 273 in the Centigrade, or 459 in the Fahrenheit scale, to the given temperature.

Calculations for Correction of Volume. Since gas volume

varies with varying conditions, it is always necessary to state the temperature and pressure at which observations are taken in speaking of gases. In statements of the density of gases, normal temperature and pressure are assumed, which is 760 m.m. of mercury in pressure, and 0° C. (32° F.). It frequently becomes necessary, therefore, to calculate the volume of a gas from a given temperature to the normal. Since the volume of a gas is directly proportional to the *absolute temperature,* the correction is easily made, as shown in the following example:

If a gas measure 50 c.c. at 40° C., its volume at 0° C. is found by the proportion:

$$50 \text{ c.c.} : (40° + 273°) :: x : (0° + 273°),$$

$$50 : 313 :: x : 273,$$

$$x = \frac{50 \times 273}{313} = 43.61 + \text{c.c., volume at 0° C.}$$

In the above calculation, the pressure is assumed to remain constant. Suppose the 50 c.c. of gas at 40° C. to be under a pressure of 730 m.m.; then, as shown above, its volume becomes 43.61 c.c. at 0° C. and 730 m.m. What the volume would become at 760 m.m. can be found by reference to Boyle's law, which says: "The volume of a gas is inversely proportional to the pressure." Therefore:

$$760 : 730 :: 43.61 : x,$$

$$x = \frac{730 \times 43.61}{760} = 41.88 \text{ c.c. at 0° C., 760 m.m.}$$

TRANSMISSION OF HEAT.

If two bodies, having different degrees of temperature, be brought in contact, the rapidly vibrating molecules of the hot body will transfer a part of their motion to the slowly-moving molecules of the colder substance, until finally, a point is reached when the velocity of their molecular vibration is the

same. The two have then reached a state known as the *mobile equilibrium of temperature,* in which they exchange equal amounts of heat. This mutual exchange of heat not only takes place between bodies in contact, but occurs in several other ways:

1. **Conduction.** If one end of an iron bar be held in the flame of the Bunsen burner, the other extremity soon becomes too hot to be borne by the hand of the operator. Conduction is this property of transmitting heat through the mass of a body, from one molecule to the next, and it is developed to different degrees in different substances. Metals are the best conductors of heat; gases and liquids, except mercury, are poor conductors. The relative heat-conducting power of different bodies is shown in the following table; taking silver as the standard of comparison:

Silver	1.000	Water	0.002
Copper	0.960	Glass	0.0005
Gold	0.530	Wool	0.00012
Iron	0.200	Paper	0.000095
Stone	0.006	Air	0.000049

2. **Convection** means carrying, or transferring heat by means of the movement of masses of molecules, and generally takes place in the movement of heated currents of gases or liquids. If a long narrow test-tube be nearly filled with water, the liquid may be boiled in the upper part of the tube while it remains cool in the lower end; thus showing the low conductivity of water. But suppose this tube be heated at its lower extremity; in that case, the heated portions of the liquid, lessening in specific gravity by expansion, rapidly rise to the surface, and, at the same time the colder portions fall to the bottom of the tube, forming rapidly circulating currents by means of which heat is evenly distributed throughout the liquid. Heat distribution, in this manner, is known as *convection.*

3. **Radiation** is the transmission of heat through space. A heated body suspended in air, or in a vacuum, will give out heat to surrounding objects. In order to explain this transmission of heat through space, as well as the phenomena of light and electricity, it is assumed that an exceedingly tenuous and elastic medium pervades all space and exists between the molecules of matter; this hypothetical substance is called *ether*. The molecular vibrations in a heated body produce corresponding oscillations, or waves, in the surrounding ether, whereby heat is radiated in straight lines in all directions from the hot body.

The Thermal Unit. The temperature of a substance expresses the degree, or intensity of heat; the quantity, or amount of heat of a body is expressed in *heat units, or calories*. A very fine platinum wire, when heated to the high temperature of redness, may yet be held between the fingers without injury because the *quantity* of heat is so small. *The thermal, or heat unit* is the quantity of heat required to raise the temperature of one pound of water from 32° to 33° F. The *calorie* is the quantity of heat required to raise the temperature of one gram of water from 0° to 1° C.; but, since 1 gram of water has proved to be too small a standard for accurate observations, the *great calorie* is generally employed, and this is the quantity of heat required to raise the temperature of 1 kilogram of water from 0° to 1° C.

SPECIFIC HEAT.

Equal weights of different substances having the same temperature require different quantities of heat to raise their temperature through the same number of degrees. Specific heat is an expression showing the quantity of heat required to raise the temperature of a given weight of a substance through a certain number of degrees, compared with the quantity of heat

required to raise the temperature of the same weight of water through the same number of degrees. The standard of comparison in expressions of specific heat is the thermal unit. The quantity of heat which will raise the temperature of a pound of water from 32° to 33° will raise the temperature of two pounds of olive oil from 32° to 33°. Hence we say the specific heat of olive oil is one-half—its resisting power to the influence of heat is one-half that of water. One pound of water at 100° mixed with one pound of water at 40°, will give two pounds of water having a mean temperature of 70°. One pound of water at 100° and one pound of olive oil at 40°, will give two pounds of the mixture having a temperature of 80°. The twenty degrees of heat lost by the pound of water, when mixed with the pound of olive oil, were sufficient to raise the temperature of the oil forty degrees; *i. e.*, from forty to eighty degrees. Therefore, the specific heat of oil is said to be 20/40, or one-half that of water. One pound of water at 100° and one pound of mercury at 40° give two pounds of mixture at 98°; according to which, the specific heat of mercury would be 2/58, or 1/29. The specific heat of a body increases as its temperature rises.

LATENT HEAT.

Liquefaction. Many solid bodies, when heated, not only expand, but when the degree of heat is sufficiently intense they become liquids. Some of these become soft and pasty just before fusing, as iron, glass, etc., while others pass directly from the solid to the liquid state, as lead and zinc. Most bodies when in the act of melting expand, but water is an exception to this rule. During melting, eleven volumes of ice form about ten volumes of water.

During the passage of a body from the solid to the liquid state the temperature remains constant until transition is complete, no matter how great the supply of heat may be. It is therefore

concluded that a certain amount of heat is absorbed by the body in changing its state of aggregation. This heat is not indicated by the thermometer, and is called *latent heat.* If a pound of water at 0° be mixed with a pound of water at 80°, a mean temperature of 40° is obtained. But if a pound of powdered ice at a temperature of 0° be mixed with a pound of water at 80°, the temperature of the two is brought to 0°; the ice, however, will have melted. It is thus seen that the heat required to convert a pound of ice at 0° to a pound of water at 0° would be sufficient to raise the temperature of a pound of water from 0° to 80°.

The production of artificial cold by freezing mixtures depends upon these physical phenomena. Whenever rapid liquefaction can be brought about, unattended by chemical change, great cold is produced. A mixture of a pound of powdered ice and salt gives a temperature of — 17.7°. Powdered crystallized calcium chloride and snow, reduce the temperature enough to freeze mercury. Rapid solution of solids in liquids also causes great reduction of temperature.

Volatilization. If a liquid be subjected to a constant source of heat, its temperature will gradually rise until the boiling point is reached, and will there remain constant in spite of continued heating. It will be noticed, however, that the liquid is being volatilized, and it is in the conversion of liquid into vapor that the heat is consumed. Whenever matter passes from the liquid to the gaseous state, a quantity of heat is absorbed, or made latent, and apparently disappears. The quantity of heat lost in the conversion of a liquid into a gas is much greater than that which disappears when a solid is converted into a liquid. One part of steam at a temperature of 100° C., in becoming water at 100° C., parts with enough heat to raise the temperature of 5.4 parts of water from 0° to 100° C., or a sufficient quantity of heat to raise the temperature of 540 parts of water 1°, if it

were possible to prevent the loss of any of the liberated heat. Whenever matter passes from the gaseous to the liquid, or from the liquid to the solid state, heat is disengaged to the same extent that it is absorbed when the opposite change occurs.

By placing water in a vessel whose sides are perfectly clean and smooth, in a room in which the air is free from particles of dust, the temperature may be greatly reduced below the freezing point, and the water remain liquid. If now, a grain of sand or small particle of other solid be dropped in, so as to form a nucleus for crystallization, ice suddenly forms and the temperature rises to 0°. A supersaturated solution of sodium sulphate can be made by making a hot saturated solution and placing it in a tightly corked bottle. When the solution cools down, it remains liquid, but when the cork is removed, or a crystal is dropped in, rapid crystallization of the salt takes place, accompanied by an appreciable rise in temperature.

Boiling. Many liquids when heated to a sufficiently high temperature are converted into vapor. When the bubbles of vapor forming within them acquire a sufficient degree of tension to overcome the cohesion of the liquid, adhesion to the vessel, and pressure upon the surface, a condition of ebullition or boiling is established. Each liquid has its own boiling point under certain given conditions, and it will be seen that these conditions are cohesion, adhesion and pressure upon the surface: by varying these, the boiling point may also be varied. The boiling point of water under ordinary atmospheric pressure is 100° C., or 212° F.

The solution of less volatile substances in a liquid raises the boiling point. Water, when saturated with common salt, boils at the temperature of 109° C.; when saturated with potassium carbonate it boils at 135° C.; and, when saturated with calcium chloride, boiling takes place at 179° C.

The boiling point is also influenced by the character of the

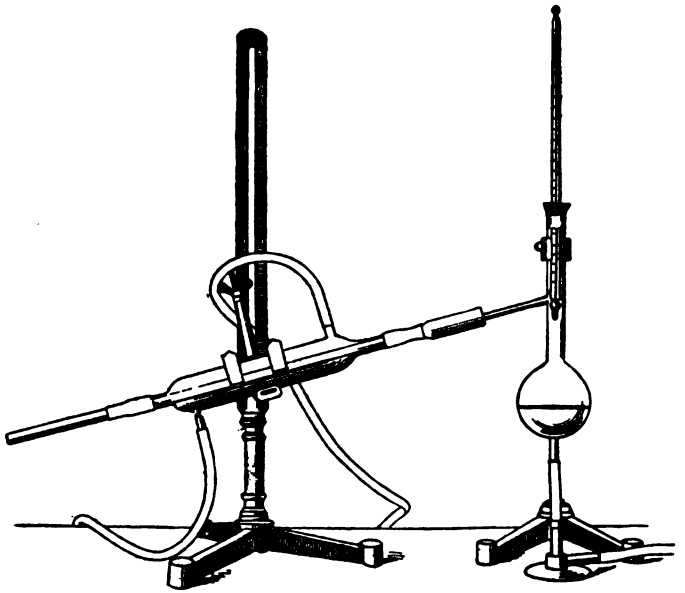
containing vessel. In a vessel having a rough metallic surface, water boils at 100° C. or slightly below this point; but if the surface be smooth and polished, as in a glass flask, the temperature often rises a few degrees above 100° C., when violent or explosive boiling takes place for a moment, the temperature then sinking to 100° C. This explosive boiling, caused by adhesion between the sides of the vessel and the heated liquid, can be prevented by dropping in a few angular fragments of insoluble solid, so as to give points from which the forming vapor may escape.

Pressure is an important factor in influencing the boiling point. When the pressure is small, as on high mountains or in a vacuum, water boils at a low temperature; but when it is increased by confining the steam, the boiling point is raised with increasing pressure. Temperature of water in a boiler at the pressure of 150 pounds to the square inch (ten atmospheres) is about 360° F. It is thus seen that pressure upon the surface of a heated liquid has a restraining influence to prevent its conversion into vapor. It has been found by experiment, however, that there is a point of temperature for each volatile liquid at which it becomes a vapor, regardless of the amount of pressure to which it may be subjected, and this point is referred to as the "*critical temperature*" of the substance.

The vapors of liquids behave in all respects like other gaseous bodies as long as they are not in contact with the liquids from which they are formed, and as long as the temperature is distant from the point of condensation. The condition of *maximum* density of a gas or vapor is that point beyond which its density cannot be increased without the gas assuming the liquid state. The increase in density of a gas is effected by two agencies, viz., pressure and cold; and when these are combined, a powerful influence is brought for the liquefaction of a gas. On account of the perfect resemblance of vapors to gases, it was

supposed that the latter could be liquefied by means of pressure and cold, and it has been found that all of the gases which were thought to be permanent, can be liquefied by this means.

FIG. 11.



Distilling Apparatus. (After Rockwood.)

Distillation. The process of distillation has for its object the separation of liquids rising in vapor at different temperatures, or the removal of a volatile liquid from a substance incapable of being volatilized. The same process, when applied to those bodies which pass directly from the solid to the vaporous condition, and back again, is called *sublimation.*

Every distilling apparatus consists essentially of a boiler, or retort, in which the substance is vaporized; and a condenser, in which the vapor is cooled, and returns to its original condi-

tion. These are made in many different forms, to suit the purposes for which they are intended.

Fractional distillation is the separation of liquids having different boiling points from a mixture of liquids, by repeatedly distilling, and collecting the vapors that come over at different temperatures.

Destructive distillation is the process of heating non-volatile organic bodies in a closed retort, so as to exclude oxygen, and collecting the volatile products which form.

LIGHT.

Light is the agent which, by its action on the retina, excites the sensation of vision. Two theories have been advanced to explain the cause of the phenomena of light. One, which was proposed and advocated by Sir Isaac Newton, is that luminous bodies emit infinitely small particles from every point of their surface, and that these, by penetrating the eye and falling upon the retina, produce the sensation of light. This theory has been abandoned, and at the present time light is believed to be caused by the vibrations of ether, or by ether waves.

Ether waves produce different results depending upon the frequency and amplitude of the vibrations; comparatively slow vibrations cause the transmission of heat, more rapid vibrations produce light, and vibrations of still greater frequency excite chemical action.

The heat waves have a rate of vibration less than 477,000,000 millions per second, and they are sometimes called infra-red rays. The vibrations in light waves extend from 477,000,000 millions to 699,000,000 millions per second; the slowest vibrations, which are the longest waves, producing red light, and then, with increasing frequency of vibration, the following colors are formed in succession: orange, yellow, green, blue, indigo and violet.

The range of wave-lengths for light of different colors is not great. Experiments indicate that the length of ether waves for red light is .0000271 of an inch, and for violet light, .0000155 of an inch.

Ether vibrations of greater frequency and smaller amplitude than occurs in the violet light, constitute a form of energy which is beyond the range of the field of vision; these are referred to as the ultra-violet, or actinic rays, and are capable of exciting chemical action.

All of the ether waves are probably the same in their essential nature, but differ only in degree; it is therefore frequently the case that they are all set in motion from one body at the same time. The sun's rays contain all these forms of energy, and are thus capable of producing heat, light and chemical action.

Color is produced by the reflection of certain constituents of white light, which go to make up the tint, while the rest is absorbed. White is produced by those bodies which reflect all of the light they receive, while black objects absorb all that falls upon them. All bodies are black when there is no light.

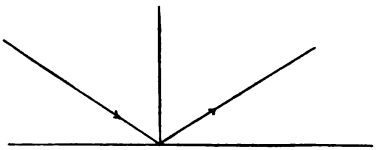
Light of itself is invisible, as may be shown by allowing a ray to pass through a dark room: if the air be free from floating particles it cannot be seen, but any substance placed in its track will become visible, or if it fall upon the eye its source will become apparent. Light, therefore, is the medium by which we see other bodies, but itself cannot be seen. The atmosphere serves a very important function in the diffusion of light, thus throwing it in all directions, and causing bodies to be visible which are not in the direct path of luminous rays. If one could stand in space, where there is no atmosphere to give light diffusion, he would be surrounded by the blackness of night, except when his eyes were turned upon the glaring orb of the self-luminous sun, or to the shining point of reflected light from some planet.

Light passes in a straight line in all directions from a luminous point as long as the medium it is traversing remains of the same density; its velocity is 186,000 miles per second. A change in the density of the medium through which the light is passing, is accompanied by a change in direction and a slight change in velocity.

Transparent bodies are those which allow the free passage of light; opacity is the property of preventing its passage; and a translucent substance allows only a small amount to pass through.

Reflection. When a ray of light falls upon a mirror or polished surface which it cannot penetrate, it is reflected into the medium from which it came. If a line be drawn perpendicular to the reflecting surface, it will be found that this line forms an angle with the incident ray, which is equal to the angle it forms with the reflected ray; therefore, we say that the angle of incidence is equal to the angle of reflection.

FIG. 12.



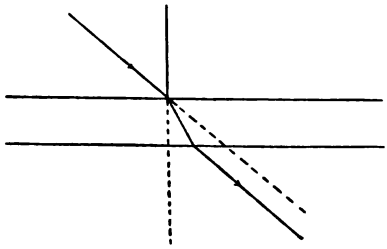
Showing Direction of a Ray of Light in Reflection.

The light reflected from visible bodies is diffused, or thrown in all directions, coming from many minute surfaces of which the exterior of the body is composed.

Refraction. A medium is a space or substance through which light is capable of passing. As long as the medium remains of the same chemical composition and density, the light travels in a straight line; but if a ray of light be passed from one medium to another of greater density, the direction of the ray is changed and the change of direction is found to be towards a line perpendicular to the surface of the medium. On emerging and passing into a rare medium, the reverse is found

to be the case, and the light is bent away from the same perpendicular line. This change of direction by bending is called refraction. The amount of refraction, or bending, increases with increasing obliquity of the incident ray. The perpendicular ray is not refracted.

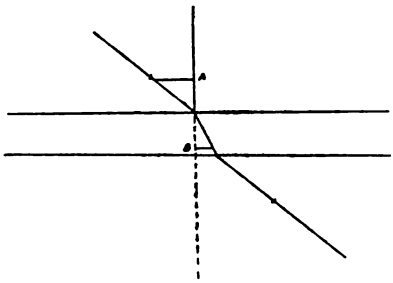
FIG. 13.



Showing Direction of a Ray of Light in Refraction.

The angle formed by the incident ray with a perpendicular, bears a constant ratio to the angle formed by the refracted ray, in each refracting substance; this ratio expresses the index of refraction for that substance. While the amount of refraction increases with increasing obliquity of the incident ray, with a given body, yet the relation between the sizes of the angles of incidence and refraction remain the same. The index of refraction expresses the relation between the sine of the angle of the incident ray (a) and the sine of the angle of the refracted ray (b), and is a fixed quantity for each substance.

FIG. 14.

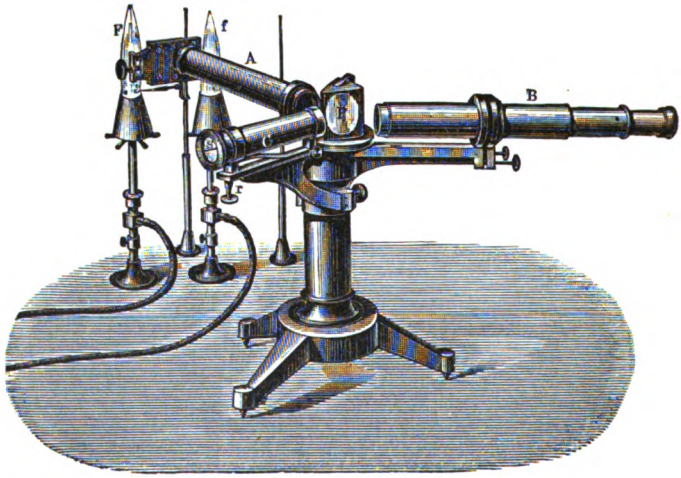


Showing Index of Refraction.

Dispersion. If a ray of light is passed through a refracting medium whose sides are not parallel, the direction in which it travels is completely changed. When light is passed through a prism its direction is changed on this account, and upon

emerging, it is dispersed, or broken up, into the colors of the rainbow. When the base of the prism is turned up, and the emergent rays are thrown upon a screen, the colors presented from above downward are, violet, indigo, blue, green, yellow, orange and red. This dispersion of white light is due to dif-

FIG. 15.



Spectroscope. (After Traube.)

ferences in the degree of refrangibility of its component parts; the violet being most refrangible, and red the least. The image formed in this way is called a *spectrum*.

The Spectroscope is an instrument used for observing the spectrum. Differently constructed instruments are used, but the one most frequently employed consists of three telescopes directed upon a prism, mounted on a stand. One of the telescopes receives the light through a narrow slit in its distal extremity, while near the other end a convex lens is fixed, called "the collimeter," which throws the light in parallel beams upon the prism. A second telescope, through which the spectrum

is observed, receives the dispersed light, and is adjusted to the observer's eye. The third tube contains a mounted scale. This scale when illuminated, casts its image on the face of the prism, and is seen by the observer just above or below the spectrum.

When light from a luminous flame is observed through the spectroscope it is found to be broken up into its constituent colors and the image is called a *continuous spectrum.*

Bright Line Spectra. If we place a salt of sodium upon a piece of platinum wire, and hold this in the non-luminous flame of the Bunsen burner, before the spectroscope, a bright yellow line will be observed in the spectrum, occupying the position held by yellow in the continuous spectrum. It will be observed at the same time that all the other parts of the spectrum remain dark; only the bright yellow line of sodium appearing. If we examine the spectra given by other elements, each one will show its own characteristic bright lines, no two appearing alike. By making use of this fact, the spectroscope can be used as an instrument of analysis. In examining metallic salts, the metals are so much more luminous than the non-metals, that only the spectra of the former are seen.

Absorption Spectra. Suppose we vary the above experiment by placing before the spectroscope a luminous flame, and then volatilize a compound of sodium, by heating it between the source of light and the instrument. The spectrum, when observed, will be continuous, except that a dark line appears in the exact position formerly occupied by the bright yellow line. We find, therefore, that while incandescent sodium vapor gives only a bright line in the spectrum; if white light be passed through sodium vapor, this bright line becomes a dark line in the continuous spectrum. We conclude, from these observations, that the kind of light waves which sodium vapor gives out when heated, will also be absorbed from white light by the vaporous metal.

Other elements, examined under similar conditions, present their own characteristic dark lines. Such spectra as these are called *absorption, or reversed spectra.*

White light from the sun, when examined by the spectroscope, shows a number of dark lines which correspond to similar appearances from such elements as iron, sodium and hydrogen. These lines are named for their discoverer, and are called *Frauenhofer lines.* These appearances in the solar spectrum lead to the conclusion that the sun consists of an incandescent central mass, surrounded by elements in the condition of vapor.

Certain parts of white light are absorbed by many substances in solution; and this action is sufficiently characteristic to permit identification of the substance. Upon this fact depends the use of the spectroscope in medicine and toxicology for the recognition of blood and solutions of organic or mineral compounds.

Fluorescence is a phenomenon which occurs as a result of change in the degree of refrangibility of light. If a solution of quinine be examined by reflected light, a pale violet color will be noticed; this is due to the power of the solution to lessen the degree of refrangibility of ultra-violet rays, thus bringing them in the field of vision. Other bodies than quinine possess this power, and some substances will change the refrangibility of light already in the field of vision. A change in degree of refrangibility is accompanied by a change in color.

Polarization. Certain transparent crystals possess the remarkable property of causing a single incident ray of light, in passing through them, to be split into two. A crystal of Iceland spar (crystallized calcium carbonate) shows this property to a very high degree and, if it be placed over a printed page, the characters underneath all appear double.

If the crystal of Iceland spar be placed over a black spot on a piece of paper, two spots will be seen, and if the paper be

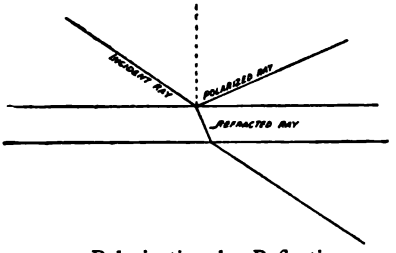
gradually turned, one spot appears to remain stationary, while the second is observed to rotate around the first. The ray of light representing the stationary spot is called an *ordinary ray;* that from the movable spot, an *extraordinary ray.*

FIG. 16.

Polarization by Refraction.

The extraordinary ray possesses unusual properties in that it does not follow the laws of reflection, refraction or transmission which govern ordinary light. A ray of light having these unusual properties is said to be *polarized.* The production of this change in the character of light by passing it through a transparent substance is *polarization by refraction.*

FIG. 17.



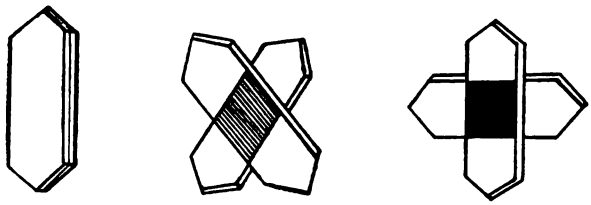
Polarization by Reflection.

Furthermore, light may be *polarized by reflection,* as may be seen by allowing it to fall upon the surface of plate glass at an angle of 54 degrees and 45 minutes. Polarization by reflection occurs whenever the line formed by the reflected ray makes a right-angle to the direction of the refracted ray.

There is one direction (sometimes two) in every doubly refracting crystal, in which light may be passed without being changed; so that an object looked at through the crystal in this direction does not appear double. A line traversing this path through the crystal is called the *optical axis.*

Some crystals which doubly refract light will absorb the ordinary ray and allow the extraordinary, or polarized, ray to pass through. The mineral tourmaline is a body possessing this property. Two plates of tourmaline, cut parallel to the

FIG. 18.



Action of Tourmaline Crystals Upon Polarized Light.

axis of the crystal, can be used to examine some of the properties of polarized light. If light be passed through one of these crystals, it is polarized; if now we place the other crystal behind the first, in a position in which their axes are parallel, the light passes without obstruction. But suppose we place the second crystal in such manner that the axes of the two are at right angles; the result will be complete obstruction to the passage of light. The first of these crystals, used to polarize the ray, is termed the polarizer, while the second, used to examine the ray, is called the analyzer.

In ordinary light, it is assumed that ether vibrations take place in every plane at right angles to the direction of the ray; but in polarized light, it appears that the vibrations are limited to one plane. This belief is based upon the peculiar action just observed with the tourmaline crystals. A piece of tightly

drawn cord will vibrate through two oblong apertures in sheets of cardboard, as long as the openings are parallel, but if they be placed at right angles, vibration ceases. This is analogous to the vibrations of polarized light through tourmaline plates.

FIG. 19.

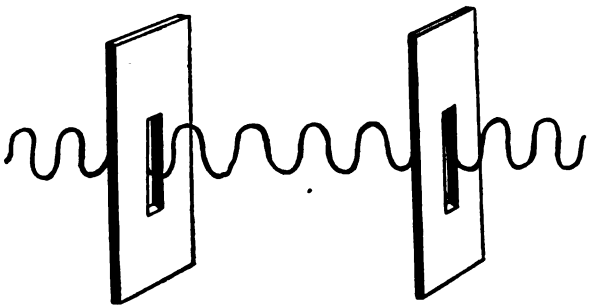


Diagram Showing Action of Tourmaline Plates.

+ **Circular Polarization.** If two polarizing crystals be placed at right angles to each other, so that light passing through the

FIG. 20.

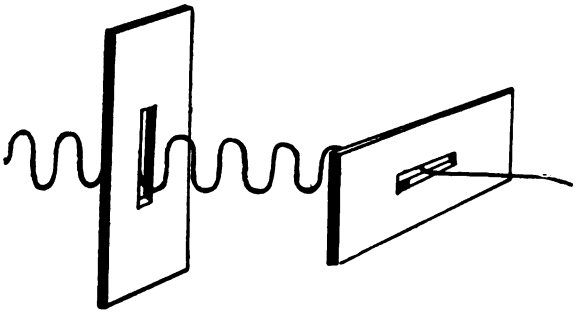


Diagram Showing Action of Tourmaline Plates.

first is completely obstructed by the second, and then a piece of rock crystal interposed between; the light will be turned, or rotated, in such manner as to pass through the crystals.

This action of the rock crystal is known as circular polarization, and it is exerted by many substances. Those which rotate to the right are called dextro-rotatory; those which rotate to the left are called levo-rotatory: both classes of bodies are said to be *optically active.*

The Polariscope, or Polarimeter, is an instrument which is used for examining polarized light. It consists essentially of two Nicol's prisms, such as have just been described. One of the prisms acts as a polarizer, and receives the light; the other is the analyzer, and can be turned through the degrees of a circle upon a disk. The substance to be examined is dissolved in a suitable liquid and placed in a glass tube. The tube, having been closed at both ends by transparent glass plates, is inserted in a horizontal position between the two Nicol's prisms upon the stand of the polariscope. The Nicol's prisms, having previously been placed so as to obstruct the light, will now permit its passage if the substance be optically active. The analyzer is then turned until light is again cut off, and the number of degrees of a circle required to effect this result indicates the amount of circular polarization of which the substance is capable.

FIG. 21.

Polariscope.

Since the amount of rotation of the ray of polarized light

varies with strength of solution and length of tube, as well as character of substance, a standard has to be adopted with regard to these factors.[1] The *specific rotatory power* of a substance may be defined, as that amount of angular rotation, expressed in degrees of a circle, produced by one gramme of substance per c.c. of volume, in a tube one decimeter in length.

Heating and Chemical Action of Different Parts of the Solar Spectrum. Reference has already been made to the action of ether waves beyond the range of the field of vision. If we now examine the different colored lights in the spectrum, by means of a delicate thermometer, it will be observed that the temperature slightly increases from the violet to the red end of the image; and when certain kinds of glass are used for the prism, the highest temperature is found to be beyond the visible red rays. The character of a substance from which the prism is made will determine to some extent the temperature of different parts of the spectrum, since many transparent bodies have the power to absorb heat. Transparent crystals of rock-salt do not possess the power to absorb heat, and the spectrum from a piece of this substance shows the highest temperature far beyond the red rays. It is thus seen that the portion of light which has the highest heating capacity is that which possesses the lowest degree of refrangibility.

The power of light to excite chemical action is a matter of common observation. Chlorine and hydrogen combine under the direct influence of sunlight; and salts of iodine, silver and many other elements are decomposed by its action. It is not always the luminous ray, however, which excites this action. That portion of the spectrum beyond the violet and out of the field of vision possesses this property in the highest degree, and

[1] Amount of rotation varies also with character of light, temperature, and character of solvent. Monochromatic light, having one wave-length and one degree of refrangibility, must be used.

the radiant energy causing this action is called the *actinic, or chemical rays.* Though the power to excite chemical action is not confined to any one part of the spectrum, yet it is more strongly developed towards and beyond the violet end. We thus see that the chemical rays possess the highest degree of refrangibility.

ELECTRICAL ENERGY.

MAGNETISM.

Certain kinds of iron ore known as magnetic iron ore, or loadstone, are found to possess the unusual property of attracting small pieces of iron, and of causing them to adhere. Bodies of this character are called natural magnets; and their power to attract is found to be most strongly developed at the extremities, which are called poles, while at the middle this power is almost entirely absent. The middle of the magnet constitutes the neutral zone.

If a piece of this loadstone be rubbed in a certain manner over a bar of steel, its properties will be communicated, and the steel will also become a magnet. Soft iron is capable of being magnetized, but its magnetism is of a temporary character, and disappears as soon as the magnetizing agent is withdrawn. The force of magnetism is not interfered with by interposing non-magnetic substances, such as paper or wood, between the magnet and the body it attracts.

If a magnetic needle be suspended by a silken thread, so as to be free to move, it will place itself in a longitudinal direction in regard to the earth; one end pointing to the north and the other to the south. The north pole of the magnet is represented by the plus sign (+), and the south pole by the minus sign (—). When two magnets are brought near together, it will be observed that the north pole of one attracts the south pole of the other; while poles of the same name repel. It is impos-

sible to separate the poles by breaking the magnet into two equal parts, for when it is broken, each piece becomes a complete magnet, having a north and a south pole of its own, however often we may repeat the subdivision.

ELECTRICITY.

When glass or sealing wax is rubbed with a dry cloth, the glass and wax acquire the power of attracting small bits of paper or feathers. These bodies, when brought into this condition, are said to be electrically excited. If a bit of feather be suspended by a fine silken thread and a piece of excited wax brought near, it will be attracted strongly by the wax and adhere to it for a moment, and then be repelled. This is due to the fact that the wax causes in the feather an electrical condition opposite to that of its own by induction, and the attraction follows. When the two bodies come in contact the kind of electricity contained in the wax is transmitted to the feather, and both having the same kind of electricity, they repel each other. If the feather, after having been charged with electricity from the wax, be brought near the excited glass, it will be attracted with much greater power than had the feather not been previously charged. These two kinds of electricity—that excited in glass and that excited in wax—are distinguished by calling the former *positive,* or *vitreous,* and the latter *negative,* or *resinous.* Two bodies charged with different kinds of electricity attract each other, but when they are similarly electrified they repel.

A body containing a charge of electricity has the power to disturb the electrical condition of surrounding objects by the process of induction. When two bodies are brought near together, and the first is given a charge of positive electricity, the electrical condition of the second is disturbed in such manner that the side next to the charged body contains negative

electricity, while positive electricity is driven to its other extremity. If the two bodies be now separated, the electrical disturbance in the second disappears; but if, instead of separating them, we make a momentary connection of the distant end of the second body with the earth, and thus allow its positive electricity to escape, it becomes charged with negative electricity. If the two bodies are separated after allowing the second to acquire a charge of negative electricity, the charge is retained; but if the two be brought in contact, the negative electricity of one neutralizes the positive electricity of the other, and electrical equilibrium is established in them both.

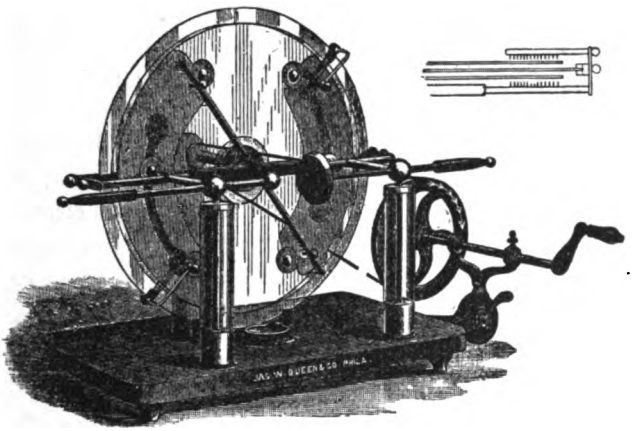
There is much resemblance between magnetism and electricity in the properties of attraction, repulsion and induction; but in addition to these, the phenomenon of discharge is observed in electrical processes. Discharge is the act by which electricity is transferred from one body to another, in order to reëstablish a condition of electrical equilibrium; it is often accompanied by the appearance of a bright spark, especially when opposed by conditions of resistance. Those materials which allow the free passage of electricity through their substance are known as *conductors,* while those which oppose or obstruct its passage are called *non-conductors, or insulators.* Examples of the first class are represented by silver, copper and most of the metals; examples of the second class are glass and rubber. *Static electricity,* is electricity at rest: *dynamical, voltaic, or current electricity,* is electricity in motion.

ELECTRICITY BY FRICTION.

The simplest form of the electrical machine, for producing electricity by friction, consists of a glass cylinder mounted upon an insulated frame. The cylinder revolves, by means of a crank, so as to rub against cushions of silk. The electricity is received upon the points of a copper comb, which convey it to a conductor of the same material.

The newer and more powerful forms of machines for generating static electricity are made so as to utilize the principle of induction. These are the Toepler-Holtz and the Wimshurst machines. The Wimshurst machine consists of two circular plates of glass, which revolve in different directions with equal velocity. Patches of tin-foil are placed upon the outer face of

FIG. 22.



Electrical Machine. (Bartley.)

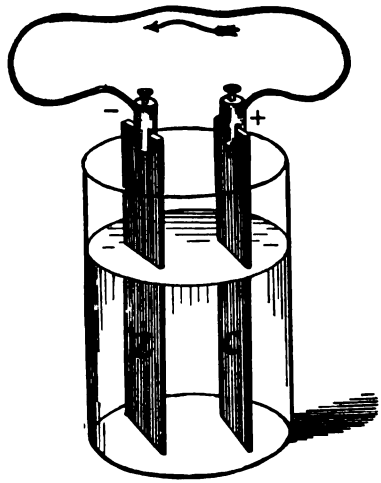
each plate at equal distances apart. Brushes of brass are so placed as to rub upon the face of the revolving glass plates, and the electricity generated is collected by horizontal brass combs, which convey it to the conductors. The machines are insulated by the use of glass stands, which prevent the escape of electricity.

ELECTRICITY BY CHEMICAL ACTION.

Electric Battery. When two solid bodies, conductors of electricity, are plunged into a liquid which acts unequally on them chemically, the electric equilibrium is disturbed; one becoming positively, and the other negatively electrified. If a

strip of zinc and a strip of carbon be partly immersed in a glass vessel of dilute sulphuric acid, the zinc plate will gradually dissolve and bubbles of hydrogen gas will escape from its surface. If, however, the two plates be connected by means of a copper wire, the hydrogen will cease to escape from the zinc plate and come off from the carbon plate. If the connecting wire be cut, and the two ends be placed on the tongue, a tingling sensation is produced; and if we bring the free ends together, so that they touch, minute sparks will be observed, and a crackling sound will be noticed. These phenomena, noticed in the connecting wire, are due to the passage of an electric current; and the arrangement described is known as a *galvanic battery*, or a *simple voltaic element*. Here we have a disturbance of electrical equilibrium by the chemical action in the battery cell, and an effort to reëstablish equilibrium by a current in the connecting wire. The zinc plate in the battery generates positive electricity, the carbon plate, negative; but positive electricity accumulates at the carbon or negative plate, and negative electricity accumulates at the zinc or positive plate, so that out of the battery the electrode from the zinc carries negative electricity, and the one from the carbon carries positive electricity. The wire coming from the carbon plate is called the positive electrode, or *anode;* from the zinc, the negative electrode, or *cathode*. The direction of the current is that which is taken

FIG. 23.



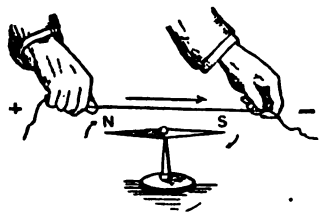
Battery Cell.

by the positive electricity, and the parts through which the current is flowing are known as the circuit. When the connecting wires from the two plates of the battery are brought together, so that the current is free to flow, the circuit is said to be closed; when they are disconnected, it is said to be open.

ELECTRICITY BY MAGNETIC INDUCTION.

Electro-magnetism. It has long been known that magnetism can be induced in steel articles by electrical discharges, but the meaning of these phenomena were not understood until they were investigated by Oersted and Ampère. If a wire conveying an electrical current be brought near a magnet which is suspended in such a manner as to be free to move, and the current be passed over the magnet from north to south, the latter will deviate from its normal position toward the east. If the current be reversed, the magnet will deviate toward the west: placing the current below the magnet produces a deviation in the opposite direction to that which it produces when placed above. When the current is made to pass around the magnet in a longitudinal direction, of course the effect produced is much greater. In view of these facts, a magnet may be used not only to indicate the presence of a current of electricity, but also to indicate its direction.

FIG. 24.



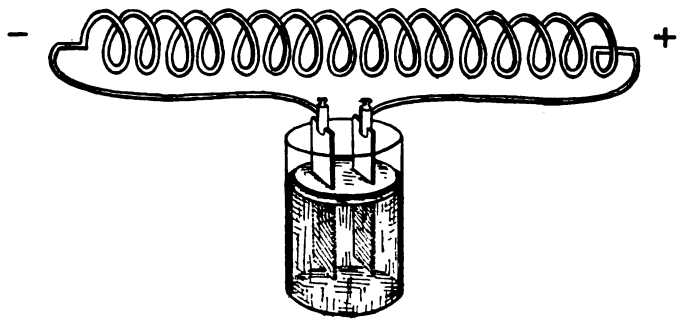
Action of Electrical Current on Magnet. (Bartley.)

Action of the Magnet on the Electrical Current. If a current be passed through a movable wire and a stationary magnet be placed under the wire, the wire will turn and place itself at right angles to the magnet. When this movable wire is placed in a direction north and south with reference to the earth, and

the current passed through it in the same direction, the magnetism of the earth will cause it to arrange itself in a direction east and west; or at right angles to a line passed through the poles—the earth being a large magnet.

Mutual Action of Electric Currents. If two wires transmitting an electric current be placed side by side, they will attract each other if the currents are passing in the same direction; if in opposite directions, they will repel.

FIG. 25.



Magnetic Behavior of an Electrified Wire Coil.

The Cause of Magnetism. If the wire be arranged in the form of a coil or helix, the coil will place itself in a direction north and south, with the direction of the current in the lower horizontal part from east to west, and thus we have an electrical magnet made of wire.

In view of these facts, magnetism is supposed to be due to the presence of electrical currents circulating in the magnetic body in a direction at right angles to its long diameter, or around its long axis; in the same manner that it is apparent in the wire coil, or helix. These currents pass in the magnet in the direction of the hands of a watch, when viewed at the south pole.

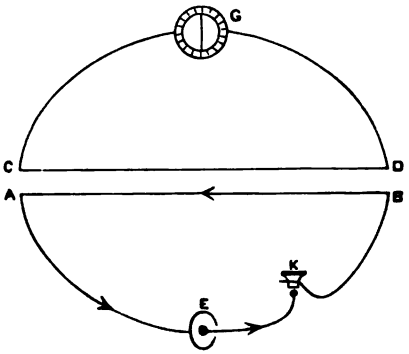
Electromagnets are formed by winding an insulated wire

many times around a piece of steel or soft iron, in a spiral manner, and passing a current of electricity through the wire. Magnetism induced in steel in this manner is permanent, and remains when the steel is withdrawn from the wire: in soft iron it is temporary, and ceases when the current stops.

The strength of an electromagnet is dependent upon the length of the wire wound around it, and the strength of the current: by using a long wire and a powerful current, magnets of great strength can be made.

Electricity Produced by Magnetism. If two wires be placed side by side, in a parallel manner, and a current of electricity be passed through one of them, a current is also momentarily induced in the second wire at the moment it starts in the first, passing in the opposite direction: when the current ceases in the first wire, a current is again induced in the second, passing in the same direction. The induced currents referred to, have a momentary duration, appearing in the second wire when the current begins and when it ends, in the other wire. In view of these facts it can be readily seen that the conditions necessary for producing a current of electricity reside in the magnet, and indeed, if a magnet be inserted within a coil of wire, a current is induced in the wire, for a moment: again, when the magnet is withdrawn, a current passes in the wire in the opposite direction. If, by some mechanical contrivance, the magnet be rapidly inserted and withdrawn from the wire

FIG. 26.



Induction of a Current in a Parallel Wire. (Bartley.)

coil, a rapidly alternating current will be set up in the wire. The equivalent of this may be accomplished in the following manner: A piece of soft iron, in the shape of a horse-shoe magnet, is wrapped many times with a coil of insulated wire. A permanent magnet is made to revolve before the ends of the soft iron, so that its poles touch the latter with each revolution. By this means the soft iron is rapidly magnetized and demagnetized, and with each revolution, alternating currents are set up in the wire coil, which may be conducted through wires leading from the extremities of the coil. It is upon this principle that dynamos are constructed, for the conversion of mechanical into electrical energy.

HEATING, LIGHTING AND CHEMICAL ACTION OF ELECTRICITY.

The chief difference between the effects of frictional and voltaic electricity depends upon a difference in tension, and amount of the current, in the two cases. Frictional electricity has a very high tension, but the quantity is comparatively small; voltaic electricity is of low tension and great quantity.

Frictional electricity produces very great physiological and mechanical disturbance, but voltaic electricity acts in a mild and continuous manner. The electrodes from a number of voltaic cells may be held in the hands without producing other effects than mild stimulation of the nerves, and slight muscular contractions.

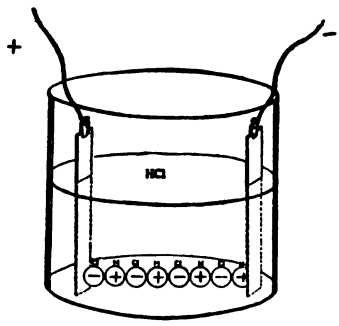
The Heating and Lighting Effects are obtained by interposing resistance in the circuit. A wire, of good conducting material and of ample size, will carry a current without appreciable elevation of temperature; but if it be a poor conductor, and of small size, the temperature is raised, and the wire may become luminous from heat. A thin wire of platinum or iron may be easily fused by the passage of a strong current. The current passed through a filament of carbon, placed in a vacuum

to prevent oxidation, gives the ordinary incandescent electric light.

Whenever the current is broken, as by cutting a wire carrying the current, the electrical spark makes its appearance; and again, when the ends of the wires are brought together, this bright light is produced. In the electric arc-light, a current is passed through electrodes of dense carbon, which are separated by a short interval. In this case, the electric spark is continuous, being formed between the electrodes.

Electrolysis. That electricity is capable of exciting chemical action, can be easily shown, by passing the current through water which has been slightly acidified with sulphuric acid. Under these conditions, the water is decomposed into its elements; hydrogen coming off at the electro-negative pole, and oxygen at the electro-positive pole of the battery. The decomposition of a substance in this manner is known as electrolysis. Since pure water cannot be decomposed by the current, the theory of electrolysis assumes that action takes place through the acid in the following manner: Sulphuric acid is decomposed into two parts, *i. e.*, H_2 and SO_4, called "*ions.*" The electro-positive ion, H_2, escapes at the negative pole; and the electro-negative ion, SO_4, passing to the positive pole, liberates its charge, takes up H_2 from water to reproduce sulphuric acid (H_2SO_4) and thus sets oxygen (O) free. The current is capable of decomposing many other salts in solution in the manner described. The salt is broken into two parts

FIG. 27.



Electrolysis of Hydrochloric Acid.

called ions, one of which goes to each pole, or electrode of the battery.

Since only those substances which are capable of forming ions are conductors of electricity in solution, it is assumed that there is a temporary dissociation of most salts when they are dissolved in water. Thus, in a solution of sodium chloride, it is assumed that there are ions of sodium and ions of chlorine, each capable of bearing its charge of electricity. In electrolysis of solutions of metallic salts, the electro-positive ion usually consists of the metal, and this is deposited on the electro-negative pole. The process of electro-plating depends upon this action. The substance to be plated is attached to the negative pole, and, when the current is passed, it gradually becomes covered with a deposit of the metal. When the positive electrode is made of the same metal as that which is being deposited, it is slowly dissolved and maintains the strength of the solution.

ELECTRICAL UNITS.

The Ohm. All bodies offer resistance to the passage of an electrical current: even good conductors show this property to some extent. In order to give expression to this fact, the term "*ohm*" is employed, and it represents the *unit of resistance.* The ohm is a term used to denote the amount of resistance afforded to the current by a column of mercury having a cross-section of one square millimeter, and a length of 106.28 centimeters, at the temperature of 0° Centigrade. For practical purposes coils of wire, having a known resistance, called *resistance coils,* are employed.

The Ampère is used to denote quantity of current. It is determined by noting the quantity of copper separated from a solution of copper sulphate, in a given time, when the current passes through. One ampère of current will deposit 0.327 milligrams of copper per second. The quantity of current is

sometimes estimated by the amount of hydrogen and oxygen separated from water in a given time.

The Volt is the unit of electro-motive force, electrical tension, or power. The volt is the pressure required to maintain a current of one ampère through a resistance of one ohm.

Ohm's Law expresses the relation existing between the three units. It is this: The strength of the current is equal to the electro-motive force divided by the resistance.

The three electrical units are named after three great electricians—Ohm, Ampère and Volta.

PART II.

CHEMICAL PHILOSOPHY.

DISTINCTION BETWEEN PHYSICAL AND CHEMICAL ACTION.

While it is difficult to define with exactness those phenomena which we class as physical, when distinguished from those termed chemical, it is easy to get a clear idea of the two by reference to a typical example of each. The effect of heat upon many different substances furnishes abundant illustration of the two kinds of action.

A piece of ice when heated is converted into water and then into steam, and when the heat is withdrawn the reverse of these changes takes place, resulting in the re-formation of ice. All such changes as these are of a temporary character, and do not affect the essential nature of the material in which they occur; they are referred to as *physical changes,* and they take place as a result of changes in the relationship of the molecules of the substance.

In other cases, heat causes a different kind of change to take place in matter. The chlorate of potassium when heated in a test-tube is completely destroyed, so that two new bodies make their appearance, one of which is a gas and the other a solid, each different from the original substance, and remaining different even when cooled. This permanent change, affecting *the essential nature,* as well as the properties of matter, occurs as the result of chemical action.

The effects of heat upon potassium chlorate give rise to the

kind of chemical action that results in decomposition. Chemical action also takes place when we mix finely powdered iron and sulphur, and then heat the mixture. The action here is so violent that heat and light are given off, and when it is over the resulting mass is found to be a new substance, differing from both iron and sulphur in its properties. The new substance, formed by union of iron and sulphur, is called iron sulphide, and the unaided senses give us no evidence whatever that it contains either iron or sulphur. It is thus seen that chemical action results in the combination of substances and the formation of new bodies, as well as in their decomposition.

For these reasons, we may say of chemical action, that it is different from all the other forms of energy, in producing an entire change in the essential nature and properties of the bodies upon which it acts. It results from changes in the relationship of certain small particles of matter called atoms.

ELEMENTS AND COMPOUNDS.

A further study of the effects of chemical action upon matter will bring clearly before the mind the fact that all of the material bodies of the universe may be placed in one or the other of the two great classes. These two classes comprise substances known as *elements,* on the one hand, and *compounds,* on the other.

Compounds. By heating the oxide of silver in a crucible to a high degree (about 250°) it is resolved into two new substances. One of these is a colorless gas, called oxygen; the other is a bright metal, silver. It is evident, from this experiment, that the oxide of silver in disappearing and being converted into the two new bodies, has been the subject of a chemical change, and we speak of the oxide by saying it is a *compound.* A compound is a body which, by chemical action, can be resolved into new substances that are unlike in their

properties. In other words, we say that a compound is a substance which can be broken up into simpler forms of matter.

Elements. If now, we proceed further with our investigations, by attempting to simplify or decompose each of the bodies produced in the above experiment, we shall discover a different kind of substance from that which has been described as a compound. Neither the oxygen nor the silver will decompose or change into simpler forms, by any means whatsoever that are known at the present time. While it is possible to add something to oxygen or to silver with which they each might unite; it still remains a fact, that neither of these bodies can be broken up into simpler forms of matter. Such bodies as oxygen and silver are, therefore, called *elements*. An element is a substance which cannot, by any of the means at present known, be broken up into simpler forms of matter.

The number of elements at the present time is said to be about seventy-eight, but the number is constantly changing. This is due to the fact that some substances which were thought to be elements, have subsequently been decomposed, and thus been found to be compounds; and furthermore, assiduous investigators, from time to time, discover a new element, which is duly added to the list.

LAWS GOVERNING CHEMICAL ACTION.

Having directed our attention first to the quality of the materials upon which chemical action manifests itself, we shall now turn to the subject of quantity as regards these materials. After decomposing the oxide of silver into its elements, we shall find that the sum of the weights of the elements equals the weight of the oxide; furthermore, we shall find the same quantity of oxygen united with a given quantity of silver in every case of analysis of the oxide.

In every attempt to form compounds, the elements will be

observed to enter into chemical union in definite quantities by weight, and not in the accidental quantities that might happen to be mixed. These facts led to the discovery of the laws of chemical combination.

A law is a statement of what has been found to be true in every case that has come under observation, and its statement implies that many cases have been studied.

1. *Law of Chemical Combination by Weight, Law of Definite Proportions, or Constancy of Composition: Each pure compound substance invariably consists of the same constituents united in the same proportions by weight.*

This law may be explained by saying that a given compound when analyzed is always found to have the same composition. For example: Calcium carbonate has of calcium, 40 parts; of carbon, 12 parts; of oxygen, 48 parts. When these ingredients are found combined in any other proportions they constitute an entirely different substance.

2. *Law of Multiple Proportions: When two elements are found to unite with each other in more than one proportion, to form separate and distinct compounds, to a constant quantity of one element the quantities of the second bear a simple multiple relation to each other.*

In order to make the law clearer, let it be assumed that A and B combine in more than one proportion to form separate compounds. In one of the compounds there is found one part of A to one part of B; in another, one part of A to two parts of B; in still another, one part of A to three parts of B, etc. Thus, carbon monoxide consists of carbon, 12; of oxygen, 16 parts; obeying the first law. But there is another compound of carbon and oxygen which contains to 12 of carbon, twice 16 of oxygen or 32 of oxygen. If there be an excess of oxygen after forming the higher compound, it does not combine, but remains mixed with the carbonic oxide. If there be not enough of

oxygen to convert all the carbon into higher oxide, the lower oxide is produced and such part of the latter is converted into higher oxide, as will satisfy the excess of oxygen present, and the two compounds remain mixed.

3. *Law of Chemical Combination by Volume, Law of Gay-Lussac: When two or more gaseous elements combine chemically to form a gaseous compound, the volume of the individual constituents bears a simple relation to the volume of the compound formed.*

Applications of this law can be seen in the following examples. One volume of hydrogen combined with one volume of chlorine, form two volumes of hydrochloric acid gas. Two volumes of hydrogen and one volume of oxygen form two volumes of steam. In other words, the relation between the volume of the compound and the volume of each of its constituents can be expressed by simple integer numbers, or whole numbers.

THE ATOMIC THEORY.

The discovery of a law naturally leads to a desire for an explanation. The question arises, Upon what condition is the existence of this law dependent? In answer to this question an explanation is given which is called an *hypothesis.* If the hypothesis is capable of offering a satisfactory explanation of all the facts, and nothing can be discovered of a contradictory nature, it then becomes a *theory.* The atomic hypothesis, proposed by Dalton soon after he discovered the law of multiple proportions (1804), has answered all the requirements.

Atoms. For each element a definite number may be selected, and these numbers, or multiples thereof, represent the proportions by weight in which the elements enter into chemical combination. The only explanation that can be offered to account for these facts is to assume that the elements combine by the union of minute particles of definite weight. These small par-

ticles of matter are called atoms. *An atom,* therefore, is a particle of matter so small as to be incapable of division by the ordinary physical or chemical methods,[1] and it represents the unit of matter in chemical changes. The properties of atoms are weight and chemical affinity. *Chemical affinity* is the force of attraction exerted by atoms upon each other, and differs from all other forms of energy in producing an entire change in the nature and properties of the bodies upon which it acts.

Molecules. On account of the force of attraction exerted between atoms they are nearly always found united in groups of two or more; in elements they usually link themselves together in pairs, the atoms being of the same kind; in compounds they are united in varying numbers of different kinds. The groups of atoms formed by such unions are called molecules (a little mass). A molecule may be further defined by saying, It is the smallest particle of matter which can exist in a free or uncombined state.

MOLECULAR CONSTITUTION OF GASES.

The doctrine that heat is the result of molecular motion is generally conceded at the present time. Observations upon gases, and liquids as well, go to show that the small particles, or molecules, of which they are composed are in a constant state of movement or agitation. With increase of temperature this molecular motion is greatly increased, and with reduction of temperature it is correspondingly retarded. At the temperature of absolute zero (273° below 0° C.) it ceases altogether.

The direction of motion in a molecule is that of a straight line until it meets with some modifying condition, such as com-

[1] Recent discoveries in regard to the properties of radio-active bodies indicate that their atoms are undergoing constant disintegration, and our ideas respecting the divisibility of atoms have to be modified accordingly. See "Radium."

pact with a fellow molecule or the sides of a containing vessel. The pressure of a gas is assumed to be due to the impacts of its molecules upon the sides of the containing vessel. Any means, therefore, by which the velocity of molecular motion is increased will increase the pressure. Thus it is observed that with an increase of temperature there is a corresponding increase in pressure, in a given volume of gas. Likewise, if a gas be made to occupy less volume, its molecules are forced closer together, and the number of impacts is correspondingly greater, giving increase in pressure (Boyle's Law). In equal volumes of different gases, under the same conditions of temperature and pressure, the number of impacts of molecules upon the sides of the vessels must be the same in each case. Since the total number of impacts, under the same physical conditions, must be proportional to the total number of molecules present, it is safe to assume that the number of molecules is the same in equal volumes. These facts are stated in *the Law of Avogadro: Equal volumes of gases, under similar conditions of temperature and pressure, contain the same number of molecules.*

The great value of this law is dependent upon the fact that it gives the means of making a direct comparison of the weights of different molecules. If we take equal volumes of two gases, under the same physical conditions, we have equal numbers of molecules. The relation of the number of molecules in the two cases is as one is to one, and a direct comparison of their weight can be made.

The behavior of gases in process of chemical union, as set forth in the law of Gay-Lussac, when viewed in the light of Avogadro's law, will give a clearer meaning to the terms atom and molecule. One volume (one molecule) of hydrogen will unite with one volume (one molecule) of chlorine to form two volumes (two molecules) of hydrochloric acid. Each volume (molecule) of hydrochloric acid contains a particle of hydro-

gen, obtained from one volume (molecule) of hydrogen; therefore, we are forced to believe that the molecule of hydrogen is made up of two atoms. Each volume (molecule) of hydrochloric acid contains also a particle of chlorine, obtained from one volume (molecule) of chlorine; showing that the molecule of chlorine is likewise made up of two atoms.

When we weigh equal volumes of two gases we are weighing equal numbers of molecules. Hydrogen gas is taken as the standard in expressing the density of a gas, but since it has been shown that the molecule of hydrogen is made up of two atoms, its molecular weight is taken as equal to two. *The molecular weight of any gas is therefore twice its density as compared with hydrogen.* The density of nitrogen is 14, its molecular weight is 28: the density of oxygen is 16, its molecular weight is 32: the density of carbon dioxide is 22, its molecular weight is 44.

One liter of hydrogen at 0° and 760 m.m. pressure, weighs .0896 gram, and is called a *crith;* a unit used in calculating gas volume from weight.

ATOMIC WEIGHT.

As far as the absolute weight of atoms is concerned, we know nothing more than we do of their size, but it is a law of nature that all matter possesses weight, and if this is true of masses of matter it must also be true of the particles which compose these masses. As atomic weights express the proportions by weight in which the elements combine with each other, the weights in which two masses enter into combination will express the relation between the weights of their atoms; presuming that the atoms link themselves together in pairs. The unit of comparison for atomic weights is hydrogen, the lightest known substance. For example, hydrogen will combine with chlorine in the proportion of one grain of the former to 35.4 grains of the latter. These numbers express their atomic weights. Atomic

weight, then, is the weight of an atom of an element expressed in terms of the hydrogen atom. The weights of the same kinds of atoms are always the same. The weights of atoms of different kinds of elements are proportional to the combining weights of these elements, *i. e.*, hydrogen, 1; sodium, 23, etc.

Atomic Weight and Gas Volume. If equal volumes of different elements, in the form of gas, under the same conditions of temperature and pressure, be weighed, these weights will be proportional to the atomic weights of the elements. We have already seen that equal volumes of gases, under the same physical conditions, contain the same number of molecules. Since it has been shown that the molecules of gaseous elements contain two atoms, the relation between volume and atomic weight, above stated, becomes clear. If we take a volume of hydrogen which weighs 1, an equal volume of nitrogen will weigh 14, of oxygen 16, of chlorine 35.4, all of which quantities represent the atomic weights of the elements named. Some elements, whose molecules contain one, or more than two atoms, show an exception to this rule.

The molecular weight of the elements is twice the atomic weight, with some few exceptions. In the case of phosphorus and arsenic, whose molecules contain four atoms, the weight is four times the atomic weight: in the case of cadmium and mercury, whose molecules contain one atom, it is the same as the atomic weight. The molecular weight of any substance may be said to be equal to the sum of the weights of the atoms in its molecule, or (with the exceptions noted) twice its density when in the form of gas.

QUANTIVALENCE, ATOMICITY, OR VALENCE.

By quantivalence is meant the combining power, or value, of one atom in relation to another, expressed in terms of the hydrogen atom. All atoms do not possess the same power of com-

bining. Sometimes one atom will completely satisfy the affinities of another, but in other cases one atom requires several others to supply its needs. An atom which requires four other atoms to satisfy its chemical affinity, is said to have four times the value of each of the others. The atom of hydrogen is said to be univalent, and is the standard of comparison. When an element requires a single atom of hydrogen to satisfy its chemical affinity, the former is said to be univalent or a monad; when it requires two, it is said to be bivalent, or a diad; when it requires three it is trivalent, or a triad; when four, quadrivalent, or tetrad, etc. Quantivalence is expressed by Roman numerals, placed to the upper right-hand side of the symbol, thus:

H^{I}, O^{II}, N^{III}, C^{IV}, S^{II}, P^{III}, Cl^{I}, Br^{I}, I^{I}, etc.

Quantivalence is also written by strokes of the pen, thus:

H', O'', N''', S'', P''', C'''', Cl', Br', etc.

While quantivalence is a sufficiently constant property to be assigned to each atom, it is not unvarying. An atom, which under usual conditions acts as a triad, is designated as such; but the same atom may under other conditions act as a pentad. Another atom, which is usually bivalent, may under other conditions act as a quadrivalent, or even as a sexivalent atom. Quantivalence, as shown in these instances, usually varies by two units or points of attraction, an atom being one, three, and five valued; or two, four, and six valued, etc.

CHEMICAL SYMBOLS AND EQUATIONS.

In making a record of the results of a chemical reaction, it would be exceedingly cumbersome and laborious to write out the name of each element concerned, and the nature of the changes they undergo. The necessity for a brief method of

writing the names of elements and compounds, and of recording their reactions, has resulted in the employment of symbols, formulas, and equations.

A Symbol consists, usually, of the first letter of the Latin name for the element. In some cases, however, the names of several elements begin with the same letter; as carbon, chlorine and calcium. In such cases, the first letter of the Latin name is assigned to the most important, or the one which has been known the longest, the others being indicated by the first and some other letter. Carbon is indicated by the symbol, C; chlorine by the symbol, Cl; and calcium by Ca.

A symbol is the first, or the first and some other letter, of the Latin name for the element. It represents the name of the element, a single atom of the element, its atomic weight, and one volume in the form of gas. If it be desired to indicate more than one atom of an element, this is done by the use of a small numeral, placed to the lower right-hand side of the symbol. Two atoms of each of the elements are indicated in the following:

$$C_2,\ H_2,\ O_2,\ N_2,\ S_2,\ P_2,\ Fe_2.$$

A Formula is a collection of symbols, and is intended to represent a molecule. A formula represents the name of the molecule, the molecular weight, and two volumes of the substance when in the form of gas.

A formula is multiplied, so as to indicate more than one molecule, by placing a full-sized numeral to the left-hand side. A molecule of hydrochloric acid is represented by the formula, HCl; two molecules of hydrochloric acid, by the formula, 2HCl, etc. It sometimes becomes necessary to indicate some multiple of a group of atoms in a molecule. Thus, the compound ammonium sulphate contains two of the group NH_4 united to the group SO_4; this fact is represented by the use of brackets, in this manner: $(NH_4)_2SO_4$. Two molecules of ammonium sul-

phate are represented by placing a full-sized numeral in front of that which stands for its molecule, thus: $2(NH_4)_2SO_4$.

An Equation represents a chemical reaction, and is composed of symbols and formulas. The formulas for the bodies entering into the reaction are placed to the left-hand side of the sign of equality, each being separated by the plus sign: the formulas for the bodies produced by the chemical reaction, are placed to the right of the sign of equality, also separated by the plus sign. The following equation represents the action of calcium carbonate upon hydrochloric acid, forming calcium chloride, water and carbon dioxide:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

An equation not only serves to indicate the character of the substances entering into and formed by a reaction, but it represents, as well, the quantity by weight of each substance concerned. If we bear in mind the functions of symbols, this can be easily understood. A symbol not only represents the name of the element and a single atom, but it also represents the atomic weight, or a quantity by weight proportional to the atomic weight. This being the case, the formula for calcium carbonate, $CaCO_3$, stands for $(Ca = 40) + (C = 12) + (O_3 = 48) = 100$, or 100 parts by weight of the carbonate. Therefore, we say, $CaCO_3 = 100$. (See table for atomic weights.) By a similar method we shall find that $2HCl = 72$; $CaCl_2 = 110$; $H_2O = 18$; $CO_2 = 44$.

The equation, written as follows, shows the quantities by weight of the different bodies entering into the reaction:

$$\begin{gathered} 100 + 72 = 110 + 18 + 44. \\ CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2. \end{gathered}$$

Viewed in this light, the equation immediately becomes the basis for calculation of chemical quantities, furnishing all the factors necessary for such calculation. Take the example:

How much hydrochloric acid is required to make 220 grams of calicum chloride?

We see by the equation that 72 parts HCl will give 110 parts $CaCl_2$:

Therefore:

$$\frac{72}{110} \times 220 = 144 \text{ gms.} \quad \text{Answer.}$$

Another method is to form the equation:

$$72 : 110 :: x : 220.$$

$$x = \frac{72 \times 220}{110} = 144 \text{ gms.} \quad \text{Answer.}$$

Example: How many liters of carbon dioxide can be obtained from 400 gms. calcium carbonate?

100 gms. $CaCO_3$ form 44 gms. CO_2, therefore:

$$100 : 44 :: 400 : x.$$

$$x = \frac{44 \times 400}{100} = 176 \text{ gms. } CO_2.$$

The next step in the problem is to find how many liters of CO_2 are represented by 176 gms. The density of CO_2 is one-half its molecular weight, or 22, as compared with hydrogen. A liter of hydrogen weighs .0896 gm.; therefore, a liter of CO_2 would weigh:

$$.0896 \times 22 = 1.9712 \text{ gm.}$$

If one liter of CO_2 weighs 1.9712 gms., 176 gms. CO_2 would be

$$\frac{176}{1.9712} = 89.28 + \text{ liters } CO_2. \quad \text{Answer.}$$

The branch of chemistry which relates to the calculation of chemical quantities is sometimes referred to as stoechiometry.

METHODS OF DETERMINING ATOMIC AND MOLECULAR WEIGHTS.

The *actual* determination of atomic and molecular weights is a matter which does not greatly concern the student of medical chemistry; he should, however, be conversant with the principles involved and the means by which the determinations are made.

Both chemical and physical means are employed in these determinations. It is customary to apply several different methods to a single substance, each method, confirming the results of the others, ensures a correct result.

Atomic Weights are determined:

1. By chemical analysis, of a compound which contains the element whose atomic weight is to be determined united to one whose atomic weight is known.

For example: Let it be desired to find the atomic weight of potassium in the compound, potassium chloride (KCl); the atomic weight of chlorine being known to be 35.5.

Analysis of potassium chloride gives the percentage formula:

Potassium	52.35%
Chlorine	47.65%
	100.00

If we remember that the quantities by weight in which the elements enter into combination are proportional to the weights of their atoms, assuming that they unite atom for atom, the following statement and equation hold true:

The quantity of chlorine is to the quantity of potassium, as the atomic weight of chlorine is to the atomic weight of potassium. Let x represent the atomic weight of potassium.

Therefore:

$$47.65 : 52.35 :: 35.5 : x.$$

$$x = \frac{52.35 \times 35.5}{47.65} = 39.$$

This method alone is not conclusive, because it does not show how many atoms of each element enter into the compound. Further experiments are then made to confirm or deny these results.

2. By replacement of hydrogen in a compound of known composition, by the element whose atomic weight is to be obtained.

If in 36 gms. of hydrochloric acid, one gm. of hydrogen were replaced by 39 gms. of potassium, we would conclude that the atomic weight of potassium is 39.

The same source of error enters here as in the first method, but the conclusions of this experiment are confirmed by taking the vapor density of potassium.

3. By taking the vapor density of the element.

It has been shown that the weight of equal volumes of the elements in form of gas are proportional to the atomic weights. The density of potassium vapor, as compared to hydrogen, is as 39 is to 1. Therefore, we have further evidence that the atomic weight is 39.

4. By relation between specific heat and atomic weight.

The fact that all atoms have the same capacity for heat is shown by the simple experiment of taking of the elements quantities by weight which are proportional to their atomic weights and heating them all alike. If we take 32 gms. of sulphur, 12 gms. of carbon, 200 gms. of mercury, and 65 gms. of zinc, and subject them all to the same source of heat, the temperature of all will be found to be the same. This is a surprising fact, seeing that we have in these quantities such widely differing amounts of matter: the quantity of mercury being greatest; the quantity of carbon being least.

The weights of the masses taken, however, are directly proportional to the atomic weights, and we have a right to assume that they represent approximately equal numbers of atoms of

each element. These observations point out a relationship between atomic weight and capacity for heat, in the elements, which has not hitherto been observed. This relationship can be more clearly expressed in terms which are set forth in the following table. The table shows that the specific heat of an element multiplied by its atomic weight gives a constant quantity which is 6.5, or a quantity closely approximating this number:

Element.	Atomic Weight.	Specific Heat.	Product.
Li	7	.94	6.6
Na	23	.29	6.7
Mg	24.4	.25	6.1
K	39	.17	6.6
Ca	40	.17	6.8

The specific heat of an element is inversely proportional to its atomic weight and, therefore, when multiplied by the atomic weight gives a constant quantity. By dividing 6.5 by the specific heat the atomic weight is obtained. These values are approximate, and some elements show exceptions to this law.

Molecular Weights are determined:

1. By chemical analysis the percentage formula is determined, and by dividing the percentage of each element by its atomic weight the relative numbers of atoms in the molecule are found.

Analysis of 100 parts of potassium chloride:

$$K = 52 \text{ per cent.} \div 39 = 1.3+ : \text{ in simplest terms } 1K.$$

$$Cl = 48 \text{ per cent.} \div 35 = 1.3+ : \text{ in simplest terms } 1Cl.$$

The results of this analysis show that the relative number of atoms of the elements is the same. The number of atoms of potassium bear a ratio to the number of atoms of chlorine that is expressed by the ratio of one to one. This analysis does not show the actual number of atoms present, but that may be determined by taking the vapor density.

2. By ascertaining the vapor density of the compound as compared to hydrogen.

The vapor density of a compound is one-half its molecular weight. If the vapor density be 37, the molecular weight would be 74; corresponding to the formula KCl (K = 39 + Cl = 35 = KCl = 74). If the vapor density be 74, the molecular weight would be 148; corresponding to the formula, K_2Cl_2 = 148.

3. By the method of Raoult.

Relations have been discovered between the freezing point of liquids and the molecular weight of dissolved solids. By dissolving solid bodies in water the freezing point is reduced below 0° C. If the solids be dissolved in quantities proportional to their molecular weights, the freezing point is lowered by an amount which is constant. For example: Assume that we have a number of bodies whose molecular weights are represented by the numbers 5, 10, 30 and 60. If we take 100 c.c. of water, in each of four vessels, and then dissolve the bodies in each in quantities proportional to the molecular weight; that is, 5 gm. in one, 10 gm. in another, etc., the freezing point will be depressed to the same extent in all. Therefore, if it require ten per cent. of a salt whose molecular weight is known to reduce the freezing point 1° C., and 20 per cent. of a salt whose molecular weight is unknown to reduce the freezing point 1° C., the ratio between the molecular weights is as 10 to 20.

Raoult's method is specially applicable to organic bodies, or to those which do not dissociate when dissolved. It is not applicable to all substances.

4. Other properties are also made use of in determining molecular weight, such as similarity in properties between bodies of known and unknown molecular weight; the property of forming similarly shaped crystals, etc.

The weight of a molecule equals the sum of the weights of its atoms.

CONDITIONS INFLUENCING CHEMICAL CHANGES.

Chemical action is induced by various forms of energy. Heat will decompose many compounds into simpler forms, or cause new combinations between elements and compounds. Light is a great factor in causing chemical action. Hydrogen and chlorine will combine; the chemical changes taking place in the green parts of plants, by which energy is stored up; decomposition of salts of silver; changes in many organic bodies, are all brought about by the action of light. Electricity causes chemical action in the electrolysis of water; the decomposition of salts in solution, in electroplating, etc.

The conditions favoring action of chemical substances upon each other are those which bring the particles of matter in close and intimate relationship.

Chemical action does not readily occur between solid bodies, and certainly never unless they are brought in very close contact, as by mixing powdered solids. In many cases powdered solids when mixed do not act upon each other unless they are moistened with a liquid in which they dissolve, or unless they are heated.

Chemical action takes place more readily between liquids, or between solid bodies dissolved in a liquid. Here the particles are brought near together, and the molecules freely intermingle. For the same reasons, chemical action is greatly facilitated by the gaseous state where molecules are constantly coming in contact.

Prediction of Chemical Reactions. No infallible rule can be laid down by which we can say in advance exactly what chemical change will occur under given conditions; this has to be determined in each case by experiment.

The action of mass is a factor in determining chemical

change, both as regards character and amount. For example: Oxygen will be removed from hot ferric oxide by passing a large quantity or mass of hydrogen over the heated oxide; but oxygen will be taken from hydrogen by bringing water in contact with a mass of red-hot iron. In other words, oxygen in each case passes to the substance having greater mass; sometimes favoring iron and sometimes favoring hydrogen.

The action of sulphuric acid on sodium nitrate forms sodium acid sulphate and nitric acid, but a large excess of nitric acid will convert sodium acid sulphate into sodium nitrate and free sulphuric acid.

We thus see that the character of chemical change is dependent upon the mass or quantity of matter entering into the reaction.

The action of mass in regard to amount of chemical change is seen when two mixed bodies reacting chemically do not completely decompose each other. Whenever an addition is made to the mixture of either of the two bodies, an additional amount of change occurs, though it may never be complete. The amount of chemical action is thus dependent upon the mass of reacting substances.

The Laws of Berthollet predict in some measure the character of a chemical change; they are:

1. *When two or more compounds are brought together in solution, and are capable of forming an insoluble body, that substance is formed and precipitated.*

2. *When two or more compounds are brought together in solution, and are capable of forming a gaseous body, that body is formed and liberated.*

Catalytic action is the property possessed by some bodies by which they facilitate chemical change in other substances without undergoing any apparent change themselves. For example: Chemical change is facilitated in potassium chlorate,

when this compound is heated to form oxygen, by adding black oxide of manganese. The black oxide of manganese undergoes no change itself, but by its presence facilitates change in the chlorate of potassium. It is very probable, however, that all bodies acting catalytically are decomposed and reproduced during the course of the reaction.

Nascent state means the moment of birth, referring to the atom. The atoms of an element are in the nascent state when they are first liberated from combination and have not had time to unite into molecules. Nascent hydrogen is hydrogen at the moment of its liberation from union with another substance. An element in the nascent state is much more active and ready to form new combinations than at any other time, because its atoms are free and have not yet united with each other to form molecules.

A Radical is an unsaturated group of atoms, which behaves in many compounds like a single atom. A radical, like an atom, is not usually found in the free state, but generally occurs linked to other radicals or atoms. The radical, NH_4, is found in all the compounds of ammonium, and behaves like a single atom of a metallic element.

Analysis means the breaking up or separation of compounds. *Synthesis* means the putting together or building up of compounds. *A Chemical reaction* is a chemical change, and it is usually brought about by the addition of a *reagent.*

NOMENCLATURE.

The names of compounds are generally descriptive of their composition or chemical structure, but it sometimes happens that a compound was named at a time when its chemical nature was not understood and such names do not give any idea of the nature of the substance. Many of the old names of compounds are retained to the present time. It is, therefore, diffi-

cult to give set rules for chemical nomenclature; a knowledge of this subject comes gradually as we proceed with our studies.

The names of compounds formed by direct union of two elements usually end in *ide,* for example: N_2O, nitrogen oxide. When the elements combine in more than one proportion the terms mono-, di-, tri-, tetra-, penta-, etc., are used to denote the different compounds, for example: N_2O, nitrogen monoxide; N_2O_2, nitrogen dioxide; N_2O_3, nitrogen trioxide, etc. When an element forms two classes of compounds the terms *ous* and *ic,* are used to distinguish between lower and higher forms of combination, such as ferrous and ferric chloride. The prefixes *mono-* and *proto-* are used to indicate lower forms of combination, and *sesqui-* and *per-* to indicate higher forms of combination.

Names of salts derived from acids having a single atom for their acidulous radical end in *ide,* that is, hydrochloric acid forms chlorides. Names of salts derived from acids whose names end in *ous,* end in *ite,* namely, sulphurous acid forms sulphites. Names of salts derived from acids whose names end in *ic,* end in *ate,* namely, sulphuric acid forms sulphates.

In pronouncing the name of a compound the metallic or basylous radical precedes that of the acidulous.

CLASSIFICATION OF COMPOUNDS.

Compounds are classified:

1. *According to reaction,* into acids, bases and neutral bodies.

Acids, when soluble, usually have a sour taste; they contain replaceable hydrogen; they usually change the color of blue litmus to red.

Bases, when soluble, have a taste of lye; they replace hydrogen in acids to form salts; they change the color of litmus from red to blue.

Neutral bodies are those which do not possess the properties of either an acid or a base, and have no action upon litmus.

Amphoteric reaction is a peculiar property observed in some bodies by which they turn blue litmus red and red litmus blue; acting both as an acid and as a base. This peculiar property is sometimes observed in the milk of carnivorous animals.

Indicators are substances employed for the purpose of determining whether a given body is acid, basic, or neutral in reaction. Litmus and phenol-phthalein are the ones most commonly used. Litmus is red in acid solution, blue in alkaline solution and is not affected by a neutral body. Phenol-phthalein is purplish-red in alkaline solution; it is colorless in acid or neutral solution.

2. *According to chemical composition.* In a general sense, any chemical compound may be correctly called a salt. The term salt, in a more restricted sense, is applied to those bodies which are formed by replacement of the replaceable hydrogen in an acid by a base, or by union of acids with bases. Salts are said to be normal, bi- or acid, basic and double, according to their molecular composition.

A normal salt is formed by replacement of all the replaceable hydrogen of an acid by a base. For example: Sulphuric acid contains two replaceable hydrogen atoms and when both of these are replaced a normal salt results. The formula for normal sodium sulphate is Na_2SO_4.

A bi- or acid salt is formed by replacement of part of the replaceable hydrogen of an acid by a base. If in sulphuric acid, one atom of hydrogen is replaced by sodium, the bi- or acid sulphate of sodium results, thus: $NaHSO_4$.

A basic salt contains more of the basic radical than is necessary to form a normal salt. An example of a basic salt is the basic lead nitrate, $PbOHNO_3$. Another view of the structure of a basic salt is to assume that it is formed by replacement of

a part of the OH radical of a base by an acid radical. For example: The hydroxide of lead, a base, has the formula, $Pb(OH)_2$; if one of the two OH radicals in this compound be replaced by the radical of nitric acid, NO_3, basic lead nitrate is formed, $PbOHNO_3$.

Double salts are formed in two ways: First, by replacement of the hydrogen of an acid by two different bases, thus: $KNaSO_4$, potassium sodium sulphate. Secondly, by linking together of two molecules, thus: $PtCl_4 2KCl$, double chloride of platinum and potassium.

Salts may have an acid, basic or neutral reaction, but basic salts usually have a basic reaction.

THE ELEMENTS.

Of the total number of about seventy-six elements known, only about one-third are of practical interest or importance. These important elements form the chief portion of the earth, contribute to the formation of plants and animals, and are used in various ways for the convenience and comfort of man.

Some of the elements are of scientific interest only, and there is some doubt in regard to the elementary character of a few.

Twelve elements enter into the composition of living beings without exception: hydrogen, oxygen, nitrogen, carbon, sulphur, phosphorus, chlorine, potassium, sodium, calcium, magnesium and iron. In addition to the elements named, the following are often present but are not always a part of the living body: iodine, bromine, fluorine, silicon, aluminum, manganese and copper.

The elements are found in all three states of aggregation, but most of them are solids. Five of the elements are gases; hydrogen, oxygen, nitrogen, fluorine and chlorine: two of them are liquids; bromine and mercury. Most of the solid elements are capable of being fused and volatilized by the action of heat.

Allotropic modification. In some few cases it has been found that an element is capable of existing in several dissimilar forms, for example: Carbon, which is usually seen as black, amorphous, solid charcoal, also occurs in the form of diamond, a beautiful, transparent crystal. This property of carbon, by which it occurs in these dissimilar forms, is called allotropism, and we speak of the diamond as an allotropic modification of carbon. Some important elements showing well defined allotropic forms are oxygen, phosphorus, arsenic and silver.

CLASSIFICATION OF ELEMENTS.

Early in the history of chemistry two distinct classes of elements were recognized on account of difference in properties. Such bodies as iron, silver and lead, having a characteristic lustre and power to conduct heat were distinguished from substances like sulphur, charcoal and phosphorus, which are devoid of these properties. Members of the first group are called metals, and members of the second group are called non-metals.

Metals have metallic lustre, are good conductors of heat and electricity, and their oxides usually form basic substances.

Non-metals do not have metallic lustre, are not good conductors of heat and electricity, and their oxides usually form acidulous radicals.

While it is easy to distinguish a metal from a non-metal when a typical member of each group is taken, there are some elements which behave in a manner that places them in an intermediate position between the groups. Such elements as these act as metals under some conditions and as non-metals under others, but these instances are not numerous, and do not interfere with the value of the system of classification.

Classification of Mendelejeff. This classification is based on the atomic weights of the elements. If we examine the list of

elements we shall find that there are groups in which there is a direct relationship between atomic weights and properties. Among these may be mentioned lithium, potassium and sodium; and chlorine, bromine and iodine. These elements arranged according to their atomic weights, appear as follows:

Li = 7,	Cl = 35,
Na = 23,	Br = 79,
K = 39,	I = 126.

If in these groups the atomic weights of the first and last members be added together and the sum divided by two, very nearly the atomic weights of the middle members are obtained. If we examine the properties of the members of each of these groups we shall find that they are very similar. Considerations of this sort have led to a careful study of the atomic weights and properties of elements to find if there is not some general relationship between these two factors, and it has been found that the connection stated above is much more general than was at first supposed.

Mendelejeff first pointed out the fact that if the light elements whose atomic weights range from 7 to 36 be arranged in the order of their atomic weights, they are also arranged in the order of their properties, as shown in the following:

Li = 7 : Be = 9 : B = 11 : C = 12 : N = 14 : O = 16 : F = 19.

Na = 23 : Mg = 24 : Al = 27 : Si = 28 : P = 31 : S = 32 : Cl = 35.

In these series it will be seen that there is a gradation of properties from left to right, the elements on the left being most basic, those on the right least basic: the power to combine with oxygen increases from left to right: the power to combine with hydrogen, being absent on the left, appears at the middle and increases towards the right. Elements which are similar in properties fall together, such as lithium and sodium, beryllium and magnesium, oxygen and sulphur, etc.

This system of classification has been found to apply to all the elements, and Mendelejeff has arranged them in the order of their atomic weights in periods of seven, the properties of the first element being found to be repeated in every eighth element. This classification is shown in the table on page 89.

It will be noted in the table that the members of the even series resemble each other, and the members of the uneven series resemble each other more closely than do the members of the even and uneven series. In other words, members of series 1, 3 and 5 are very much alike, and the same can be said for the members of series 2, 4 and 6. On the other hand, members of series 1 and 2, or 2 and 3, or 4 and 5 are not very much alike. It will be further seen that following the even series 4, 6 and 10 there are groups of elements which hold an intermediate position and constitute an eighth group to themselves.

A small period comprises a series of seven elements. A large period comprises an even and an uneven series with the intermediate group.[1]

[1] The student will be better prepared to comprehend the full meaning of this system of classification after he has studied the properties of the different elements.

MENDELEJEFF'S TABLE OF CLASSIFICATION (from Richter's Inorganic Chemistry).

		I Group.	II Group.	III Group	IV Group.	V Group.	VI Group.	VII Group.	VIII Group.		
H-Compounds. Highest Salt-forming Oxides.		— M_2O	— MO	— M_2O_3	MH_4 MO_2	MH_3 M_2O_5	MH_2 MO_3	MH M_2O_7	MO_3	MO_2	MO (M_2H)
Periods.	Series.										
I	1st	Li 7	Be 9	B 11	C 12	N 14	O 16	Fl 19			
II	2d	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.4			
III	3d	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Ni 59	Co 59
	4th	Cu 63	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 80			
IV	5th	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	— 100	Ru 102	Rh 103	Pd 106
	6th	Ag 108	Cd 112	In 114	Sn 118	Sb 120	(?)Te 127	I 126. 5			
V	7th	Cs 133	Ba 137	La 138	Ce 140	(Pr 140, Nd 144)	—	Sa 150	—	—	—
	8th	—	—	—	—	—	—	—			
	9th	—	—	Yb 173	—	Ta 183	W 184	—	Os 191	Ir 193	Pt 195
	10th	Au 197	Hg 200	Tl 204	Pb 207	Bi 208	—	—			
		—	—	—	Th 232	—	U 239	—			

TABLE OF ELEMENTS.

	Symbol.	Atomic Weight.[1]		Symbol.	Atomic Weight.[1]
Aluminum	Al	26.9	Neodymium	Nd	142.5
Antimony	Sb	119.3	Neon	Ne	19.9
Argon	A	39.6	Nickel	Ni	58.3
Arsenic	As	74.4	Nitrogen	N	13.93
Barium	Ba	136.4	Osmium	Os	189.6
Bismuth	Bi	206.9	Oxygen	O	15.88
Boron	B	10.9	Palladium	Pd	105.7
Bromine	Br	79.36	Phosphorus	P	30.77
Cadmium	Cd	111.6	Platinum	Pt	193.3
Caesium	Cs	131.9	Potassium	K	38.86
Calcium	Ca	39.8	Praseodymium[4]	Pr	139.4
Carbon	C	11.91	Radium	Ra	223.
Cerium	Ce	139.2	Rhodium	Rh	102.2
Chlorine	Cl	35.18	Rubidium	Rb	84.8
Chromium	Cr	51.7	Ruthenium	Ru	100.9
Cobalt	Co	58.56	Samarium	Sm	148.9
Columbium[2]	Cb	93.3	Scandium	Sc	43.8
Copper	Cu	63.1	Selenium	Se	78.6
Erbium	Er	164.8	Silicon	Si	28.2
Fluorine	F	18.9	Silver	Ag	107.12
Gadolinium	Gd	155.	Sodium	Na	22.88
Gallium	Ga	69.5	Strontium	Sr	86.94
Germanium	Ge	71.9	Sulphur	S	31.83
Glucinum[3]	Gl	9.03	Tantalum	Ta	181.6
Gold	Au	195.7	Tellurium	Te	126.6
Helium	He	4.	Terbium	Tb	158.8
Hydrogen	H	1.000	Thallium	Tl	202.6
Indium	In	113.1	Thorium	Th	230.8
Iodine	I	125.90	Thulium	Tm	169.7
Iridium	Ir	191.5	Tin	Sn	118.1
Iron	Fe	55.5	Titanium	Ti	47.7
Krypton	Kr	81.2	Tungsten	W	182.6
Lanthanum	La	137.9	Uranium	U	236.7
Lead	Pb	205.35	Vanadium	V	50.8
Lithium	Li	6.98	Xenon	Xe	127.
Magnesium	Mg	24.18	Ytterbium	Yb	171.7
Manganese	Mn	54.6	Yttrium	Yt	88.3
Mercury	Hg	198.5	Zinc	Zn	64.9
Molybdenum	Mo	95.3	Zirconium	Zr	89.9

[1] H = 1.000 (U. S. Pharmacopoeia, Eighth Decennial Revision).
[2] Also called Niobium, Nb.
[3] Also called Beryllium, Be.
[4] Also called Didymium, Di.

PART III.

INORGANIC CHEMISTRY.

THE NON-METALLIC ELEMENTS.

The number of the non-metals is about eighteen, but of these, helium, argon, selenium and tellurium are of little importance and will receive only a brief mention in this book.

Most of the important non-metals are solids, one is a liquid and five are gases at the ordinary temperature.

Non-metals do not possess metallic lustre, except iodine; they are not conductors of heat or electricity; their oxides usually form acids; they are electro-negative.

HYDROGEN.

Symbol, H. Atomic Weight, 1. Quantivalence, I.

History. Hydrogen was prepared by Paracelsus in the sixteenth century, but its true character was established by Cavendish in 1766, who found it to be a peculiar gas, and gave it the name "inflammable air."

Occurrence in Nature. Hydrogen occurs in comparatively small amount in the free state, being found in the intestinal gases and in gases issuing from the earth. It occurs in abundance in combination in water, in the bodies of plants and animals, in ammonium compounds and in acids.

Preparation. Hydrogen can be obtained in a pure state by passing a current of electricity through water which has been acidified with sulphuric acid. It can be prepared, also, by the

action of metallic sodium upon water, as shown in the equation:

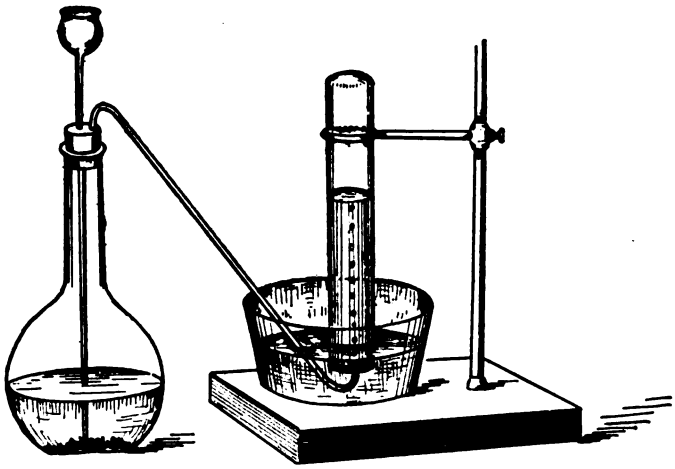
$$\underset{\text{Sodium}}{Na} + \underset{\text{Water}}{H_2O} = \underset{\text{Sodium hydroxide}}{NaOH} + \underset{\text{Hydrogen}}{H}.$$

The usual method of preparation consists in adding dilute sulphuric acid to fragments of zinc in a glass vessel, and allowing the gas to escape through a delivery tube, it is then collected over water. The reaction is represented by the following equation:

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Hydrogen}}{H_2}.$$

Hydrogen, and many other gases, are collected by taking a vessel, filling it with water and inverting it in another vessel filled with the same liquid. The delivery-tube, from which

FIG. 28.



Preparation of Hydrogen.

hydrogen is escaping, is carried under the edge of the inverted vessel and the gas rises, displacing the water until a vesselful is obtained. When a gas to be collected is soluble in water, some other liquid is employed, such as mercury.

Properties. Hydrogen is a colorless, odorless, tasteless, inflammable gas; it is the lightest known substance, being 14.4 times lighter than air. One liter of hydrogen at 0° C., 760 mm. mercury, weighs .0896 gm.; this unit has been referred to as the *crith.*

By compressing the gas to 180 atmospheres, cooling it by surrounding with liquid air boiling in a vacuum, and suddenly reducing the pressure to 40 atmospheres, hydrogen has been obtained as a transparent, colorless liquid. Certain metals, such as iron, platinum and palladium, when heated to redness, have the power to absorb large volumes of hydrogen, forming compounds which have some resemblance to alloys; this property is referred to as *occlusion.* On account of the same property hydrogen is capable of passing through the substance of hot metals.

Hydrogen burns in the air with production of a high degree of heat, with a non-luminous flame of slightly bluish color; it does not support combustion or respiration, but can be breathed without danger for a short time, imparting a peculiar piping tone to the voice. A mixture of air, or oxygen, with hydrogen will explode violently when ignited. The oxy-hydrogen flame is produced by combustion of a mixture of oxygen and hydrogen in a peculiarly constructed burner, wherein the gases are brought together at the moment they undergo ignition. This flame is non-luminous and gives a high degree of heat: if it be caused to fall upon a mass of unslaked lime the latter becomes incandescent, and emits the well-known " calcium light."

Experiment. Place a few fragments of zinc in a large test-tube, add enough water to cover the zinc and then a few drops of sulphuric or hydrochloric acid. Fit a delivery tube, wait for air to be expelled and collect the hydrogen over water.

Examine the gas and confirm the properties given above. Notice that the gas is combustible and not a supporter of combustion. Reserve two small test-tubes full of the gas. Complete the equations:

$Zn + H_2SO_4 =$ $Zn + 2HCl =$.

How many grammes of hydrogen may be obtained from 50 grammes of sulphuric acid? How many liters?

Water is produced by the combustion of hydrogen, and it can be collected in drops by holding a cold surface over the hydrogen flame. In its chemical relations, hydrogen shows some resemblance to metals, being found in all acids, and its place being substituted by a metal in forming a salt.

OXYGEN.

Symbol, O. Atomic Weight, 16. Quantivalence, II.

History. Discovered by Priestley, in England, and Scheele, in Sweden, in 1774. Lavoisier, in France, first explained the chemical behavior of oxygen in reference to combustion and respiration.

Occurrence in Nature. Oxygen is the most abundant element in nature; probably one-third of the weight of the earth is made up of this element. It occurs free in the air; in combination, it occurs as a constituent of most mineral and organic bodies, and in water.

Preparation. Oxygen can be made by heating the oxides of mercury, gold, silver or platinum, or by heating potassium bichromate with sulphuric acid.

The usual method of preparation consists in heating together potassium chlorate and black oxide of manganese, in a test-tube, to which a delivery tube has been fitted, and collecting the gas over water. If potassium chlorate be heated alone oxygen will be given off at a high temperature, but the chemical action is facilitated by the presence of black oxide of manganese, the gas coming off at a lower temperature. This is an instance of " catalytic action," the quantity of black oxide of manganese being the same before and after the experiment.

Properties. A colorless, odorless, tasteless gas; density sixteen times that of hydrogen; solubility in water, about three

volumes in 100 at ordinary temperature. A colorless liquid at temperature of — 140° and pressure of 300 atmospheres. Boils at — 180° at pressure of atmosphere.

Chemically, oxygen is a very active element, and combines directly with nearly all elements except Cl, Br, I, F, Au and Pt: it combines with these indirectly, except fluorine. The direct union of bodies with oxygen, with the evolution of heat and light, is called combustion. Oxidation of bodies in air without evolution of light is called slow combustion. Combustion in pure oxygen takes place with great intensity: the red-hot wick of an extinguished candle or a piece of glowing charcoal will burst into flame and burn with a brilliant light, when plunged into the gas.

The union of oxygen with another body is called oxidation, and it is not always necessary for the oxygen to be in a free state, for some substances are capable of giving oxygen to others. A substance capable of thus giving up its oxygen is called an oxidizing agent. A body taking the oxygen is called a deoxidizing or reducing agent. Chlorine may act as an oxidizing agent in the presence of moisture by uniting with hydrogen and liberating the oxygen with which it was combined.

Oxygen is the constituent of the atmosphere which actively supports the respiration of animals; but it occurs here diluted with four-fifths of its volume of nitrogen, being too active when in the pure state. An animal placed in an atmosphere of pure oxygen shows great stimulation of all the vital functions for a time, but it soon expires from overstimulation and exhaustion, due to the rapid oxidation of its tissues. Oxygen is used in medicine by inhalation in those diseases which reduce the surface of absorption of oxygen from the air, such as tuberculosis and pneumonia; it is used also for the temporary sustentation of life in some cases of impending dissolution.

Experiment. Place a small quantity of a mixture of equal parts of potassium chlorate and black oxide of manganese in a large test-tube, fit the delivery tube and heat carefully. Collect the escaping oxygen

over water and observe its properties. Oxygen is not combustible but it is a supporter of combustion. Mix a small test-tubeful with two small test-tubefuls of hydrogen in a large test-tube. When the mixture is ignited explosion takes place with formation of water. Complete the equation:

$$2KClO_3 + \text{heat} = \quad .$$

How many grammes of oxygen can be obtained from 10 grammes of $KClO_3$? How many liters?

Ozone.

Formula, O_3. Molecular Weight, 48.

Ozone is an allotropic modification of oxygen. It was discovered in 1840 by Schönbein.

Preparation. Ozone can be obtained by the passage of non-luminous electrical discharges through oxygen or air; also by oxidation of phosphorus partly covered with water.

Properties. Ozone is a gaseous body, having slightly bluish tinge when viewed in large quantity, the odor of fresh eggs and a density one-third greater than that of oxygen. It can be liquefied by pressure, and when heated to about 237° is converted into oxygen.

On account of its density ozone is said to have three atoms to the molecule, instead of two as found in ordinary oxygen. It is more active as an oxidizing agent than oxygen, and in the act of oxidation one atom combines with the body attacked, while the other two atoms are given off as ordinary oxygen. Ozone decomposes iodide of potassium with liberation of iodine, and may be recognized by moist strips of paper saturated with potassium iodide and mucilage of starch, giving a blue color.

COMPOUNDS OF OXYGEN WITH HYDROGEN.

These elements unite in two proportions: Hydrogen monoxide, or water, H_2O; and hydrogen dioxide, or peroxide, H_2O_2.

WATER.

Formula, H_2O. Molecular Weight, 18.

Water, as found in nature, is never in an absolutely pure condition. It contains impurities derived from the atmosphere and impurities derived from the soil.

Impurities commonly found in water and derived from air are the gases, oxygen, nitrogen, and carbon dioxide, also traces of nitrate and sulphate of ammonium. Impurities derived from the soil are sodium chloride; chlorides, carbonates, and sulphates of calcium, magnesium and potassium. *Hard water* contains comparatively large quantities of these salts, especially the carbonates and sulphates of calcium. *Temporary hardness* is that which is due to the presence of calcium carbonate held in solution by carbonic acid gas. When the water is boiled temporary hardness disappears because the carbonic acid gas is expelled and the calcium carbonate is precipitated. *Permanent hardness* is due to salts dissolved in the water, chief of which are calcium sulphate and chloride; these do not precipitate upon boiling.

Mineral waters contain a sufficient quantity of salts to impart a decided taste or to impart medicinal properties. The chief varieties of mineral waters are designated in the following terms: *Bitter waters* contain the sulphate and chloride of magnesium. *Chalybeate waters* contain iron carbonate or sulphate. *Sulphur waters* contain hydrogen sulphide and sulphides of calcium, magnesium and potassium. *Effervescent waters* contain carbon dioxide. *Alum waters* contain the sulphate of aluminum and potassium. *Lithia waters* contain the salts of lithium, usually the carbonate.

In order to obtain water in a state of purity it has to be subjected to distillation. The first and last portions are rejected, in distilling water for its purification, in order to insure the absence of foreign matter.

Drinking water should not be chemically pure, but should contain from 3 to 5 parts of dissolved mineral matter in 10,000 parts of water and a small percentage of carbonic acid gas, about one per cent. by volume. The presence of this small percentage of dissolved mineral and gas gives palatability and lightness to the water, which would have a "flat," insipid taste if it were chemically pure. The presence of *organic matter* in drinking water renders it unwholesome and dangerous to health.

Properties. Water is odorless, tasteless, blue in deep layers, can be volatilized by heat and solidified by cold. Temperature of greatest density of water is 4° C. The solvent power of water is very great, it being more largely used as a solvent than any other liquid. Its solvent power is increased by heat except in the case of a few salts, such as sodium chloride and some of the salts of calcium.

Water is a neutral body, but it combines with some oxides to form acids, and with some other oxides to form bases. *A hydroxide,* formerly called a hydrate, contains the radical OH. *A hydrous body* is one which contains water. *An anhydrous body* is one which does not contain water. *An anhydride* is a body which by union with water forms an acid.

The crystalline character of many salts is due to the presence in a solid state of a certain number of molecules of water. This water is referred to as the *water of crystallization,* and when it is driven off by heat the crystal falls to powder.

A salt, when it loses water of crystallization by exposure to air is said to undergo *efflorescence.* Some other salts when exposed to air absorb moisture and are partly or completely liquefied; this property is known as *deliquescence.* The term *hygroscopism* means power to absorb moisture from the air, and it is usually applied in speaking of liquid or organic substances.

Hydrogen Peroxide.

Formula, H_2O_2. Molecular Weight, 34.

Preparation. Prepared by acting upon barium dioxide with an acid, and carefully evaporating the product in a vacuum at a low temperature. The following equation shows the action of sulphuric acid upon barium dioxide:

BaO_2	+	H_2SO_4	=	$BaSO_4$	+	H_2O_2.
Barium dioxide		Sulphuric acid		Barium sulphate		Hydrogen peroxide

Hydrogen peroxide may also be obtained by action of carbon dioxide and water upon barium dioxide, as shown in the following:

CO_2	+	H_2O	+	BaO_2	=	$BaCO_3$	+	H_2O_2.
Carbon dioxide		Water		Barium dioxide		Barium carbonate		Hydrogen peroxide

The insoluble barium sulphate or carbonate, as the case may be, is separated by filtration, and the filtered liquid evaporated in a vacuum.

A solution of hydrogen peroxide can be prepared, for use in cases in which the presence of a sodium salt does not interfere, by adding an acid to sodium dioxide, Na_2O_2, and water.

Properties. Pure hydrogen dioxide is a colorless, odorless, corrosive, oily liquid; specific gravity 1.45; freely soluble in water, glycerine or ether. It bleaches organic coloring matter, and easily decomposes into oxygen and water.

The commercial liquid, so largely used in medicine as an antiseptic, is a solution in water of about 3 per cent. strength, slightly acid in reaction, having all the properties of the peroxide except that it is not oily nor corrosive. The term " volume solution " refers to the number of volumes of oxygen that can be obtained from one volume of the commercial liquid. A ten volume solution is 3 per cent. by weight of H_2O_2.

Tests. 1. Strips of paper saturated with solution of potassium iodide and mucilage of starch give a blue color with hydro-

gen dioxide, due to the fact that the dioxide liberates iodine which turns blue when in contact with starch.

2. Peroxide of hydrogen is decomposed by silver oxide with liberation of oxygen, according to the equation:

$$\underset{\text{Silver oxide}}{Ag_2O} + \underset{\text{Hydrogen peroxide}}{H_2O_2} = \underset{\text{Silver}}{Ag_2} + \underset{\text{Oxygen}}{O_2} + \underset{\text{Water}}{H_2O}.$$

3. Acidified solution of potassium permanganate is decolorized by peroxide of hydrogen with evolution of oxygen.

4. Potassium dichromate added to peroxide of hydrogen which has been acidified with sulphuric acid gives a blue color, and the mixture when shaken with ether separates into two layers; blue perchromic acid formed in the reaction dissolves in the ether.

NITROGEN (Azote).

Symbol, N. Atomic Weight, 14.

Quantivalence, III and V.

Occurrence in Nature. Nitrogen is found in the free state in abundance in the atmosphere, of which it constitutes four-fifths. Compounds of nitrogen are found in animal tissues, in plants, in ammonia, in nitrates, nitrites and hyponitrites.

Preparation. By heating ammonium nitrite, according to the equation:

$$\underset{\text{Ammonium nitrite}}{NH_4NO_2} = \underset{\text{Water}}{2H_2O} + \underset{\text{Nitrogen}}{N_2}.$$

Prepared in an impure state by burning phosphorus in a confined portion of air over water whereby the oxygen is exhausted, leaving nitrogen.

Properties. A colorless, odorless, tasteless gas, fourteen times heavier than hydrogen. At a temperature of — 146° and pressure of 33 atmospheres it is a colorless liquid, which boils at — 194° at pressure of atmosphere. Nitrogen is not combustible nor a supporter of combustion, and is characterized

by its inertness, or lack of affinity for other elements. It can be made to unite with other elements, however, by indirect means, but many of its compounds are prone to decompose, and some do so with explosive violence. The presence of nitrogen in the atmosphere serves to dilute the oxygen, and thus render it fit for respiration.

FIG. 29.

Preparation of Nitrogen.

Experiment. Place a piece of phosphorus upon cork floating in water. (Phosphorus must be cut under water and not held in the fingers, since the warmth of the hand is sufficient to cause it to ignite.) Ignite the phosphorus by touching it with a heated glass rod. As the phosphorus burns, invert a beaker over the cork. The burning phosphorus removes oxygen, and when the white fumes of phosphoric oxide have been absorbed by the water nitrogen remains. Examine its properties. Notice that it is neither combustible nor a supporter of combustion.

The Atmosphere consists chiefly of a mechanical mixture of nitrogen and oxygen, about four-fifths of the former and one-fifth of the latter, as follows:

Nitrogen, 76.99 parts by wt., or 79.22 parts by volume.

Oxygen, $\frac{23.01}{100.00}$ parts by wt., or $\frac{20.78}{100.00}$ parts by volume.

Besides nitrogen and oxygen the air contains watery vapor, carbon dioxide, traces of ammonium nitrate, hydrogen peroxide, ozone and solid suspended particles of dust.

Argon. Discovered in the atmosphere by Lord Rayleigh and Professor Ramsey in 1894. Air contains about one per cent. of this element. It is a colorless gas and has been liquefied. Chemically, it is very inert, having little or no affinity for other bodies. Symbol, A. Atomic weight, 40.

Krypton, neon and *xenon* are elements similar to argon which have been recently discovered in the atmosphere, but they are of so little importance that their names only will be mentioned.

Helium. First discovered in the solar spectrum. Occurs in many minerals, in the gases given off from some springs, and in the air. Discovered in 1895 by Professor Ramsey. Properties like argon. Atomic weight, 4. Symbol, He.

COMPOUNDS OF NITROGEN WITH HYDROGEN.

AMMONIA.

Formula, NH_3. Molecular Weight, 17.

Occurrence in Nature. Ammonia is formed in nature by the decomposition of nitrogenous organic matter, and from this source escapes into the atmosphere. It occurs in small amounts in combination with acid radicals in the form of ammonium compounds.

Preparation. By destructive distillation of nitrogenous organic matter and passing the gaseous product into water which dissolves the ammonia. In the manufacture of coal gas by destructive distillation of coal, large quantities of ammonia are formed, and by passing the gaseous product of this distillation through water the ammonia is dissolved out. Such water is known as the "ammoniacal liquor of the gas works," and is the chief source from which ammonia and its compounds are obtained.

Ammonia can be liberated from ammonium compounds by the action of a strong alkali, as indicated in the following equation:

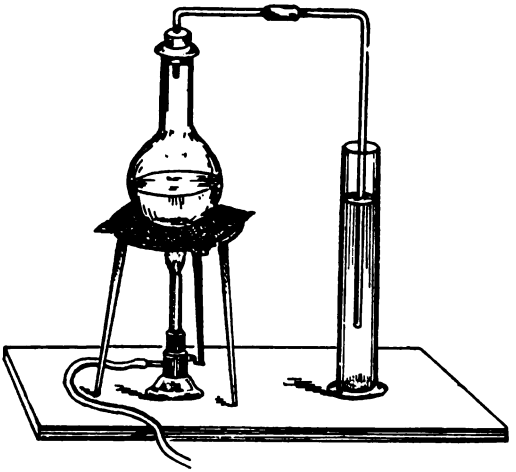
$$\underset{\text{Ammonium chloride}}{NH_4Cl} + \underset{\text{Sodium hydroxide}}{NaOH} = \underset{\text{Sodium chloride}}{NaCl} + \underset{\text{Water}}{H_2O} + \underset{\text{Amm onia}}{NH_3}.$$

Ammonia gas must be collected over mercury instead of water on account of its great affinity for the latter substance.

Properties. Colorless gas, suffocating odor, alkaline taste and reaction. Ammonia is easily converted into a liquid by a

pressure of 6.5 atmospheres at 10°, or by simply reducing the temperature to —40°. It has great affinity for water and dissolves in this liquid with such energy as to cause considerable elevation of temperature: 730 volumes of the gas

FIG. 30.



Preparation of Ammonia.

dissolve in one of water at 15°. Ammonia is not combustible nor a supporter of combustion; when inhaled it acts as a caustic irritant to the air passages.

A mixture of oxygen and ammonia is explosive. Chlorine will burn in ammonia gas. Ammonia is a strongly basic substance, as shown by its action upon litmus paper, its strongly alkaline taste and its power to combine with acids to form salts. The manner in which ammonia combines with acids is peculiar in the fact that the hydrogen of the acid is retained, with the formation of an ammonium compound, as shown by the following equation:

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrochloric acid}}{HCl} = \underset{\text{Ammonium chloride}}{NH_4Cl}.$$

When ammonia is dissolved in water a compound is formed having the formula NH_4OH, known as ammonium hydroxide, or hydrate, and having properties similar to those of the gas. A solution of this character, having 10 per cent. by weight of ammonia and a specific gravity of .958, is official in *Aqua Ammonia* (*Spirit of Hartshorn*). *Stronger Water of Ammonia,* also official, contains 28 per cent.; specific gravity, .897.

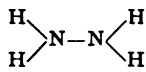
For ammonia tests, see ammonium.

Experiment. Place a little ammonium chloride in a dry small test-tube and add a few drops of sodium or potassium hydroxide and warm. Ammonia gas is given off. Complete the equation:

$$NH_4Cl + NaOH =$$

Observe the odor of ammonia, its action on a piece of moist red litmus paper held over the open end of the tube, and observe the dense white fumes produced when a glass rod moistened with hydrochloric acid is brought over the end of the tube.

Hydrazine, Diamine, N_2H_4. A compound obtained from ammonium sulphocyanate, of interest because it forms some important organic derivatives. It is a colorless, pungent gas, easily liquefied and solidified. In chemical properties it resembles ammonia, forming a hydrate of the composition $N_2H_4H_2O$. Its graphic formula is represented thus:



COMPOUNDS OF NITROGEN WITH OXYGEN.

Nitrogen forms five oxides and three acids, as follows:

Nitrogen monoxide, N_2O—Hyponitrous acid, HNO.

Nitrogen dioxide, N_2O_2, or NO.

Nitrogen trioxide, N_2O_3—Nitrous acid, HNO_2.

Nitrogen tetroxide, N_2O_4, or NO_2.

Nitrogen pentoxide, N_2O_5—Nitric acid, HNO_3.

Nitrogen Monoxide.

Formula, N_2O. Molecular Weight, 44.

Synonyms. Nitrous oxide, laughing gas.

Nitrogen monoxide was discovered by Priestley in 1776; its anaesthetic properties were discovered by Sir Humphrey Davy in 1800; and it was first used as an anaesthetic in dentistry by Doctor Wells, of Hartford, Connecticut, in 1844.

Preparation. The gas is prepared by heating ammonium nitrate to a temperature of 250°, as shown in the following equation:

$$\underset{\text{Ammonium nitrate}}{NH_4NO_3} = \underset{\text{Nitrogen monoxide}}{N_2O} + \underset{\text{Water}}{2H_2O}.$$

Properties. A colorless, odorless gas, of sweetish taste, easily liquefied by a pressure of 30 atmospheres at 0°, or by 50 atmospheres at the ordinary temperature, and the liquid boils at —80°. Nitrous oxide supports combustion almost as actively as oxygen, and when inhaled produces exhilaration and insensibility. It is largely used as an anaesthetic in dentistry. When nitrous oxide is to be used as an anaesthetic it should be caused to pass through a solution of caustic potash and ferrous sulphate in order to remove impurities. The pure compound can usually be obtained from the manufacturer in the liquid state in cast-iron cylinders.

Experiment. Place in a dry, large test-tube a small quantity of ammonium nitrate, apply heat cautiously and collect the gas over water. Observe that it is a colorless gas, of sweetish taste and supports combustion. It is used for anaesthesia in dentistry. Complete the equation:

$$NH_4NO_3 + \text{heat} = \quad .$$

Nitrogen Dioxide is a colorless gas, given off when nitric acid acts on metals. It takes up oxygen immediately on coming in contact with the air and is converted into *nitrogen tetroxide,* which is a reddish brown poisonous gas at the ordinary temperature.

Nitrogen Trioxide, or nitrous anhydride, is a dark-blue liquid at a temperature of $-20°$. When the temperature is raised above this point it decomposes into NO and NO_2.

Experiment. Place a few fragments of metallic copper on the bottom of a test-tube and add a few drops of nitric acid. Nitrogen dioxide escapes as a colorless gas, and combining with more oxygen from the air, forms nitrogen tetroxide (N_2O_4), a gas of deep red color, which is poisonous.

Nitrogen Pentoxide, nitric anhydride, N_2O_5, is produced by the action of phosphoric oxide on nitric acid, as shown in the equation:

$$\underset{\text{Nitric acid}}{2HNO_3} + \underset{\text{Phosphoric oxide}}{P_2O_5} = \underset{\text{Nitrogen pentoxide}}{N_2O_5} + \underset{\text{Metaphosphoric acid}}{2HPO_3}.$$

Nitric anhydride forms colorless crystals, which are very unstable, and sometimes undergo decomposition with explosive violence. It has powerful affinity for water, with which it combines to form nitric acid, HNO_3.

The first, third and fifth of the above oxides have their corresponding acids, produced theoretically by adding a molecule of water to each.

Hyponitrous acid, HNO, is a very unstable white solid, which decomposes into the oxide and water. It forms compounds called hyponitrites.

Nitrous acid, HNO_2, is not known in the pure state but exists in solution and in its salts, the nitrites. These two acids, hyponitrous and nitrous, are formed in nature by the oxidation of ammonia, and their presence in drinking water indicates previous contamination with nitrogenous organic matter.

Nitric Acid.

Formula, HNO_3. Molecular Weight, 63.

Synonyms. Hydric nitrate, aqua fortis.

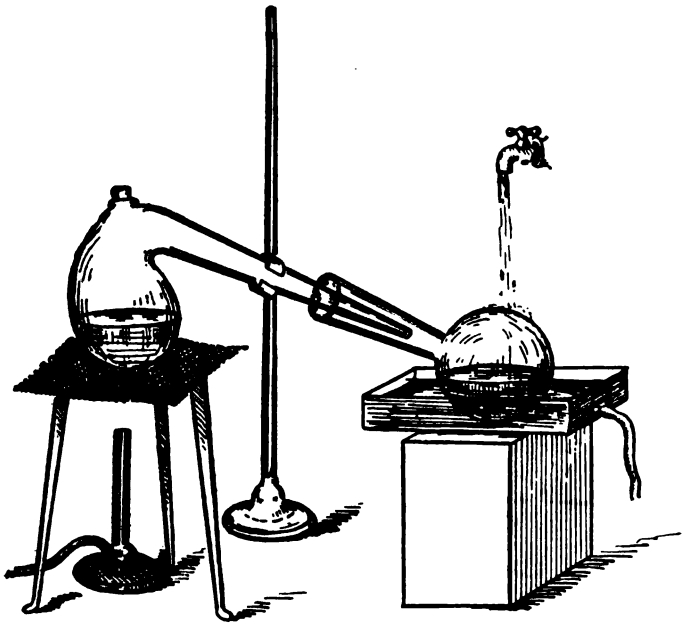
First prepared in the eighth century by distilling saltpeter with alum.

Nitric acid is formed in nature by oxidation of the product of decomposition of nitrogenous organic matter, and is found as nitrates in some soils in Chili and India. The formation of deposits of nitrates in the soil is due to the decomposition of nitrogenous organic matter into ammonia, which in turn is oxidized into nitric acid; the acid, by union with bases present, forms nitrates. Nitric acid is formed in traces in the atmosphere by electrical discharges.

Preparation. Nitric acid is prepared by distilling a mixture of sodium nitrate and sulphuric acid, according to the following equation:

$$\underset{\text{Sodium nitrate}}{2NaNO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Nitric acid}}{2HNO_3} + \underset{\text{Sodium sulphate}}{Na_2SO_4}.$$

FIG. 31.



Preparation of Nitric Acid.

Properties. When pure, a colorless, fuming, corrosive liquid, which turns brown by exposure to light because of the formation of nitrogen tetroxide, oxygen and water. The acid has a powerful affinity for water, but it may be obtained in the anhydrous state by distilling from strong sulphuric acid.

The ordinary official acid contains 68 per cent. of absolute acid and has a specific gravity of 1.403. The acid is completely volatilized by heat; it stains organic matter yellow; it is a powerful oxidizing agent. Nitric acid combines with bases to form nitrates, all of which are soluble. The diluted acid contains 10 per cent. by weight of pure HNO_3, and has a specific gravity of 1.054.

Poisonous Properties. Nitric acid, taken undiluted, acts as a powerful corrosive irritant poison, producing a yellow discoloration of the tissues. The antidote in case of poisoning is sodium carbonate, lime water, or other weak alkali, and demulcent drinks. The stomach pump should not be used, since there is danger of perforating the corroded wall of the stomach.

Tests for Nitric Acid and Nitrates.

1. Nitrates heated with sulphuric acid and copper filings, or nitric acid heated with copper filings, give off fumes of nitrogen dioxide, which become reddish brown in contact with air.

2. Solution of indigo is changed to yellow by nitric acid, or by nitrates to which sulphuric acid has been added.

3. Nitrates deflagrate when heated on charcoal.

4. To solution of a nitrate add ferrous sulphate; when sulphuric acid is poured down the side of the test-tube a brown color is produced at the line of contact of the two liquids.

5. Pyrogallic acid added to the solution of a nitrate, and sulphuric acid poured down the side of the test-tube produces a deep brown coloration at the line of contact of the two liquids.

6. Add solution of diphenylamine in strong sulphuric acid

to solution of a nitrate, and pour sulphuric acid down the side of the test-tube, a deep blue color is formed at the line of contact of the liquids.

Detection of Impurities. Evaporate some of the acid in a glass vessel; it should be completely volatilized without residue, showing absence of mineral impurities. Hydrochloric acid may be detected by silver nitrate; sulphuric acid by barium chloride. Test for iodine by diluting with water and adding mucilage of starch.

CARBON.

Symbol, C. Atomic Weight, 12. Quantivalence, IV.

Occurrence in Nature. Carbon is found in abundance in the free state in the form of graphite or plumbago, turf and coal, and in smaller quantity in the diamond. It occurs in the form of combination in all organic bodies, in carbon dioxide and in the form of carbonates in many minerals, such as marble, dolomite, limestone, etc.

Properties. Carbon occurs in three allotropic modifications which differ greatly in properties. *Diamond* is a beautiful, transparent, crystalline solid, consisting of pure carbon. It is the hardest substance known, and is converted into carbon dioxide by heating in an atmosphere of oxygen. *Graphite, plumbago, or black lead* is a dark-gray mineral, having a slight metallic lustre. It is used for making lead pencils, crucibles, as a lubricant and as stove polish. *Amorphous carbon,* a black solid, is found as coal, as lampblack and the various kinds of charcoal.

Carbon is a solid, infusible, insoluble body; permanent in the air. When heated to the high temperature of the electric furnace it softens and volatilizes to a very slight extent.

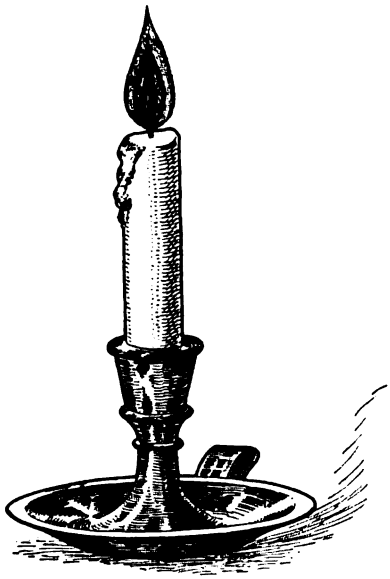
Carbon has little affinity for other elements, but at a high temperature it combines with some of the metals to form carbides, and by indirect means it can be made to unite with many of the non-metals. When heated in air or oxygen it burns,

forming carbon dioxide; and at elevated temperatures it is capable of removing oxygen from other bodies, thus acting as a powerful reducing agent.

COMPOUNDS OF CARBON WITH HYDROGEN.

These compounds are exceedingly numerous, and form derivatives with most of the other elements. They were formerly thought to be produced only in the bodies of plants and animals, and their classification into *Organic Compounds* is still retained. Organic compounds will be studied subsequently, but the following are of interest at present:

FIG. 32.



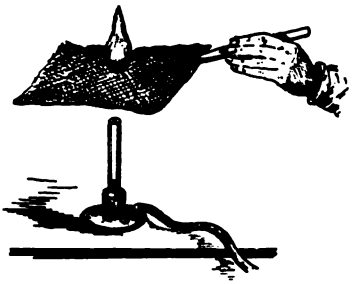
Structure of Flame.

Methane, Marsh Gas, CH_4; *Ethene, Olefiant Gas,* C_2H_4; and *Acetylene,* C_2H_2, are produced in the destructive distillation of coal, and are present in illuminating gas along with hydrogen (H) and carbon monoxide (CO). They are colorless, combustible gases.

Flame is a jet of the above gases undergoing the act of combustion. In the case of a solid the heat of combustion produces the gases, which undergo rapid oxidation. The flame consists of three cones: an inner or central cone containing unburnt gases, because the oxygen is unable to reach that part; a second, or middle cone, enveloping the former, in which the gases

are partially burnt and burning, this cone contains particles of free carbon, because the hydrogen of the burning gases appropriates most of the available oxygen, and the carbon particles being heated to a high temperature are very luminous;

FIG. 33.

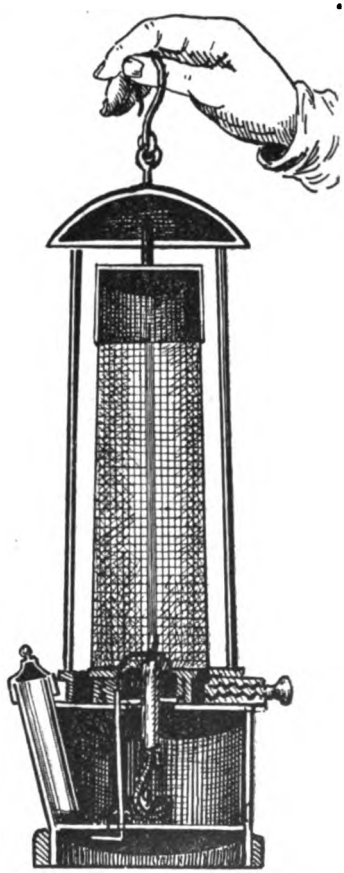


Action of Wire Gauze on Flame.

a third, or outer cone, enveloping the others, in which the gases undergo complete oxidation, giving off the largest amount of heat and almost no light. The *oxidizing* flame is the non-luminous part; the *deoxidizing,* or reducing flames, is the luminous part.

Temperature of Ignition is the point of temperature at which a substance will take fire in air or oxygen. This temperature varies with different bodies, and in combustible substances it is maintained by the burning body. The vapor of carbon bisulphide is set on fire by a heated glass rod at a tem-

FIG. 34.



Sir Humphrey Davy's Safety Lamp. (Sectional View.)

perature of about 149°, while ordinary coal-gas does not take fire when brought in contact with a red-hot iron rod. Slow oxidation of course takes place at much lower temperatures.

If a mixture of coal-gas and air be passed through an iron tube, and ignited, it will burn at the extremity of the tube, because the conductivity of the metal keeps the temperature of the gases inside the tube below the igniting point. This principle is illustrated in the *Bunsen burner,* which consists of a metal tube, through which gas is permitted to flow, with openings for air near the bottom. By means of this arrangement complete oxidation takes place throughout the flame, producing a high degree of heat and no light.

Davy's Safety Lamp. The principle of the safety lamp is shown by holding a piece of wire gauze, having about 700 meshes to the square inch, over a jet of gas. The gas when ignited above the gauze will burn there without taking fire underneath; each mesh of the gauze acts as a fine metal tube and reduces the temperature of the gas below the point of ignition so that the flame cannot pass through.

The Davy safety lamp consists of an oil lamp, having an ordinary flame, surrounded by a covering of fine wire gauze. If this lamp be placed in a combustible gas, the flame cannot pass to the outside of the gauze, though the gas may burn on the inside.

COMPOUNDS OF CARBON WITH OXYGEN.

Carbon Monoxide, Carbonic Oxide.

Formula, CO. Molecular Weight, 28.

Carbon monoxide is produced by incomplete combustion of carbon, or by the passage of carbon dioxide (CO_2) over red-hot charcoal (C). The action of carbon dioxide on red-hot charcoal is shown in the equation:

$$\underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Carbon}}{C} = \underset{\text{Carbon monoxide}}{2CO}.$$

It is also formed by conducting watery vapor over red-hot charcoal, thus:

$$\underset{\text{Water}}{H_2O} + \underset{\text{Carbon}}{C} = \underset{\text{Carbon monoxide}}{CO} + \underset{\text{Hydrogen}}{H_2}.$$

The gas formed in this way is known as water-gas; it is used as such for heating purposes, and when mixed with hydrocarbons it is largely employed for illumination.

Properties. Carbon monoxide is a colorless, almost odorless, tasteless gas. It is highly combustible, burning with a pale blue flame, forming carbon dioxide. The gas when inhaled acts as a poison by forming a compound with the hemoglobin of the blood which prevents the absorption of oxygen.

Conditions favoring the formation of carbon monoxide are present in fireplaces and stoves; in these, the coal is oxidized in the lower part of the grate into carbon dioxide, and this gas in passing upward over red-hot coals is reduced to carbon monoxide. At the surface of the grate, carbon monoxide comes in contact with the air and burns with a pale blue flame. On account of the formation of this gas under these conditions, cases of poisoning have occurred in close rooms with imperfect draft and ventilation.

Formic Acid, H_2CO_2, which would result theoretically from the union of carbon monoxide with water, thus:

$$CO + H_2O = H_2CO_2,$$

is an organic acid and is not produced in this manner. It is formed by oxidation of methyl alcohol, and will be studied in the section on organic chemistry.

Carbon Dioxide (Carbonic Acid), Carbonic Acid Anhydride.

Formula, CO_2. Molecular Weight, 44.

Occurrence in Nature. Carbon dioxide is constantly being formed in nature by the combustion of carbon or its compounds, and by the respiration of animals. It is found in the air, in water and in the soil.

The constant formation of this gas would probably result in its accumulation in the air if it were not being used up in the economy of nature. It is absorbed by members of the vegetable kingdom through their leaves and other green parts in plant respiration, the plant giving out oxygen in exchange, which serves to sustain animal life. Carbon dioxide is also taken up in the mineral kingdom in the disintegration of certain soils, forming carbonates.

Preparation. This compound is easily obtained by the action of acids upon carbonates, and collecting over water. The action of sulphuric acid upon calcium carbonate is a convenient method, as shown in the equation:

$$\underset{\text{Calcium carbonate}}{CaCO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Calcium sulphate}}{CaSO_4} + \underset{\text{Water}}{H_2O} + \underset{\text{Carbon dioxide}}{CO_2}.$$

Properties. A colorless gas; pungent odor and taste; acts as a poison when inhaled by exclusion of oxygen and interfering with exchange of gases in the lungs. Its density as compared with hydrogen is 22. The gas can be reduced to a liquid by a pressure of 38 atmospheres at 0°, and to a white solid by rapid evaporation of this liquid. It is not combustible nor a supporter of combustion, but it has the power to extinguish flame.

Carbon dioxide is soluble in an equal volume of water at the ordinary temperature and pressure of the air, and its solubility is greatly increased by increase of pressure. Ordinary "soda water" is a solution of the gas in water under pressure.

A solution of carbon dioxide in water forms carbonic acid, according to the equation:

$$\underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Water}}{H_2O} = \underset{\text{Carbonic acid}}{H_2CO_3}.$$

Carbonic Acid, H_2CO_3, has never been separated in a pure state, but decomposes into water and carbon dioxide when this

is attempted. It is presumed to be present in solution in water, imparting feebly acid properties to the liquid. It is a weak dibasic acid, whose hydrogen can be replaced by most metals, forming carbonates.

Tests for Carbonates.

1. A strong acid added to a carbonate produces effervescence, due to escape of carbon dioxide (CO_2).

2. The carbon dioxide liberated in the above test produces a turbidity, or milkiness, when passed through lime water, due to precipitation of calcium carbonate.

3. Solutions of carbonates or carbon dioxide precipitate most of the heavy metals in the form of carbonates.

SILICON.

Symbol, Si. Atomic Weight, 28. Quantivalence, IV.

Occurrence in Nature. Found very widely distributed in nature in all soils in the form of silicon dioxide, SiO_2, in sand, rock crystal, quartz and agate. Found as silicates, in which silicic acid has entered into combination with metals, in soils and rocks. Found also in the stalks of certain plants.

Preparation. By heating silicon fluoride with metallic sodium.

Properties and Uses. Silicon shows much similarity in properties to carbon, existing in three allotropic modifications. It burns when heated in air, forming silicon dioxide, SiO_2. The dioxide is the only oxide known, it is an acid oxide, forming silicates with basic metallic oxides. Nearly all silicates, except silicates of the alkalies, are insoluble in water and acids.

Sodium silicate (soluble glass) is employed for making casts in the treatment of fractures of bones of the extremities. A thick solution of the salt is rubbed into each layer of bandage as the latter is applied. This dressing forms a rigid casing for the limb as soon as its moisture has evaporated.

Test for Silicates.

Silicates may be recognized by fusing them with a mixture of the carbonates of sodium and potassium, dissolving this soluble glass in water and adding hydrochloric acid, which precipitates the silicon as a gelatinous powder of hydroxide. By evaporation of the above mixture completely to dryness on the water bath, and treating the dry residue with water acidulated with hydrochloric acid, the silicon is completely separated, remaining as a white powder of silicon dioxide.

BORON.

Symbol, B. Atomic Weight, 11. Quantivalence, III.

Occurrence in Nature. Boron is not found in nature in the free state but occurs in combination in the form of boric acid or sodium borate, dissolved in the water of inland lakes, or in volcanic lagoons.

Preparation and Properties. By heating boron trioxide with metallic sodium, sodium borate and free boron are produced; when this mixture is washed with water sodium borate is removed, leaving boron as the residue, which must be carefully dried to prevent its taking fire in the air.

Boron is a greenish-brown amorphous powder, which takes fire when heated in the air forming boron trioxide, B_2O_3. It is acted on by the oxygen acids, oxidized by water vapor, and combines with nitrogen when heated. Fused alkalies and chlorine attack it readily, the former yielding borates.

Boric Acid, Boracic Acid.

Formula, H_3BO_3. Molecular Weight, 61.54.

This acid occurs in nature in combination as sodium borate; it occurs in the free state in the hot volcanic lagoons of Tuscany.

Preparation. Prepared by evaporating and crystallizing the

naturally occurring solution, or by treating hot solution of sodium borate with sulphuric or hydrochloric acid, from which crystals of boric acid separate on cooling. The equation shows the formation of boric acid from sodium tetraborate, the naturally occurring salt:

$$\underset{\text{Sodium tetraborate}}{Na_2B_4O_7.10H_2O} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Sodium chloride}}{2NaCl} + \underset{\text{Boric acid}}{4H_3BO_3} + \underset{\text{Water}}{5H_2O}.$$

Properties. Transparent, colorless, shining, scaly crystals; soluble in about 18 parts of water, more soluble in hot; soluble in alcohol. On boiling the aqueous solution much of the acid is volatilized and lost. When boric acid is heated to 100° it loses one molecule of water, and is converted into metaboric acid, HBO_2; when further heated to about 140°, it is converted into tetra-boric acid, $H_2B_4O_7$; and when heated to redness it forms boron trioxide, B_2O_3, the only oxide of boron.

Boric acid is a feeble acid, the normal salts of which are not known. Meta- and tetra-boric acids form borates. Tetraborate of sodium, borate of sodium, or borax, is the most important salt, and will be studied with the compounds of sodium.

Tests for Boric Acid and Borates.

1. Borate of sodium heated in the flame on a loop of platinum wire forms the borax bead.

2. Add to a borate some strong sulphuric acid and a little alcohol and ignite; the flame has a greenish tinge.

3. A solution of a calcium, barium, or silver salt added to a solution of a borate gives a white precipitate.

SULPHUR.

Symbol, S. Atomic Weight, 32. Quantivalence, II.

Occurrence in Nature. Sulphur was well known to the ancients because it occurs in nature in abundance in the free state. It is found in the crevices of volcanic craters and in

volcanic districts. Compounds of sulphur occur in small quantities in the bodies of animals; they occur in abundance in the mineral kingdom as sulphates and sulphides of the metals. Sulphur occurs also as hydrogen sulphide in sulphur waters and in volcanic gases.

Preparation. The element is prepared by subliming the crude sulphur found in nature, and further purified by washing and drying the sublimate.

Properties. When pure it is a pale-yellow, brittle solid; odorless and tasteless. Sulphur, when crystallized from a solution of bisulphide of carbon, forms rhombic octahedral crystals; the form in which it is usually seen. When melted and allowed to cool slowly, it forms prismatic crystals. By heating to a temperature of about 230° and pouring into water, a brown, plastic, amorphous variety is obtained.

Sulphur is almost insoluble in alcohol and ether, but easily dissolves in bisulphide of carbon and ethereal oils. It melts into a yellow liquid at 115°, which becomes viscid at 250°; when further heated it becomes again liquid, at about 300°, and boils at about 440°, giving an orange-yellow vapor. It burns when heated in the air (260°) with formation of sulphur dioxide, but can be distilled when air is excluded. In its compounds sulphur shows much resemblance to oxygen, and forms sulphides with most of the metals.

Varieties of Sulphur. *Sublimed sulphur,* or *Flowers of sulphur,* made by subliming sulphur. A yellow, finely crystalline powder. *Washed sulphur,* made by washing the sublimed variety with weak ammonia water and then with pure water. *Precipitated sulphur,* made by boiling sulphur with calcium hydrate and water, and precipitating the resulting solution of calcium sulphide and polysulphides with hydrochloric acid, washing and drying the precipitate. In this variety the sulphur is in a very pure and finely divided state. *Roll-Sulphur,* or *Brimstone,* made by melting sulphur and pouring it into moulds.

COMPOUNDS OF SULPHUR WITH HYDROGEN.

Hydrogen Sulphide, Hydrosulphuric Acid, Sulphuretted Hydrogen.

Formula, H_2S. Molecular Weight, 34.

Occurrence in Nature. This compound is found in the gases issuing from volcanoes, and in sulphur waters; it is formed during the decomposition of organic matter containing sulphur, contributing largely to the offensive odor of putrefaction.

Preparation. Hydrogen sulphide is prepared by the action of a mineral acid upon a metallic sulphide. A convenient method of preparation consists in adding water and sulphuric acid to fragments of ferrous sulphide, the escaping gas being collected over water. This reaction is represented by the equation:

$$\underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Ferrous sulphide}}{FeS} + \underset{\text{Water}}{xH_2O} = \underset{\text{Ferrous sulphate}}{FeSO_4} + \underset{\text{Hydrogen sulphide}}{H_2S} + \underset{\text{Water}}{xH_2O}.$$

Properties. Hydrogen sulphide is a colorless gas, having a disagreeable and offensive odor. At the ordinary temperature, and a pressure of 14 atmospheres, it condenses to a colorless liquid; it burns in the air with a blue flame, forming water and sulphur dioxide; it acts as a reducing agent on account of its affinity for oxygen; it is soluble in about three volumes of water, conferring its properties upon the latter, and forming a weak acid solution; its salts are called sulphides, most of which are insoluble. Hydrogen sulphide is a valuable reagent, and it is frequently used in chemical analysis.

When inhaled, the gas acts as a powerful poison, producing insensibility and asphyxia. The best antidote is fresh air, and very dilute chlorine obtained by moistening a towel with dilute acetic acid and sprinkling the inside with a few grains of bleaching powder.

Tests for Hydrogen Sulphide.

1. A solution of salts of lead, copper, silver, or mercury gives a black precipitate with hydrogen sulphide or soluble sulphides.

2. By treating a solid sulphide with dilute hydrochloric or sulphuric acid hydrogen sulphide is given off, and may be recognized by its odor. Strips of paper moistened with solution of lead acetate turn black when brought in presence of the gas. In order to apply the above test to ferric sulphide, the sulphide of mercury, platinum, or gold, zinc must be added to the mixture of acid and sulphide.

Hydrogen Persulphide, H_2S_2, corresponds in composition to hydrogen dioxide, and is made in a similar way.

It is prepared by pouring a solution of calcium persulphide into dilute hydrochloric acid:

$$CaS_2 + 2HCl = CaCl_2 + H_2S_2.$$

The hydrogen persulphide separates as a bad-smelling, yellow, oily liquid; insoluble in water, and easily decomposed into H_2S and S.

Bisulphide of Carbon, CS_2, also known as carbon disulphide, is formed by the direct union of the two elements. It is made by passing sulphur vapor over red-hot charcoal, and condensing the vapors in a cool receiver. In properties, it is a colorless, volatile, inflammable, refractive liquid, having a peculiar disagreeable odor. Carbon bisulphide solidifies at $-116°$, and boils at $47°$; it is not soluble in water, but mixes with ether and alcohol; it dissolves sulphur, phosphorus, caoutchouc, fatty oils and resins; it burns with a blue flame, forming carbon dioxide and sulphurous anhydride.

COMPOUNDS OF SULPHUR WITH OXYGEN.

The sulphur oxides and acids of practical interest are as follows:

SO_2, Sulphur Dioxide.

SO_3, Sulphur Trioxide.

The acids:

$SO_2 + H_2O = H_2SO_3$, Sulphurous Acid.

$SO_3 + H_2O = H_2SO_4$, Sulphuric Acid.

$H_2S_2O_7$, Pyrosulphuric Acid.

$H_2S_2O_3$, Thiosulphuric Acid.

Sulphur Dioxide (Sulphurous Oxide, Sulphurous Anhydride).

Formula, SO_2. Molecular Weight, 64.

Sulphur dioxide occurs in nature in the gases issuing from volcanoes.

Preparation. It is formed by burning sulphur in the air, or by the combustion of bodies containing sulphur, such as hydrogen sulphide or bisulphide of carbon.

The gas is usually obtained by the action of sulphuric acid upon charcoal, or, in a purer state, by the action of the same acid upon the metals copper, mercury, or silver. It is collected over mercury. The equations show the action of sulphuric acid upon copper and upon charcoal:

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$
$$C + 2H_2SO_4 = CO_2 + 2H_2O + 2SO_2.$$

In properties sulphur dioxide is a colorless gas, with a suffocating, disagreeable odor; it condenses to a colorless liquid at a pressure of two atmospheres, or at — 10°, and solidifies at — 60°.

The gas has the power of extinguishing flame, and acts as a poison when inhaled; it is a strong bleaching, disinfecting and deoxidizing agent; it is very soluble in water (about 43 volumes in one of water), imparting its properties to the latter, and producing a solution of sulphurous acid.

Sulphur dioxide is used as a bleaching and disinfecting agent: in order to be effective for these purposes the presence of water is necessary.

Sulphurous Acid, $H_2SO_3 = 82$, has not been separated in a pure state but occurs in solution in water or in the form of its salts.

The acid is prepared by passing sulphur dioxide into water. The official acid is a colorless acid liquid, containing 6 per cent. by weight of SO_2, and having the odor and chemical prop-

erties of the anhydride. Sulphurous acid is dibasic, and forms normal and bi- or acid sulphites.

Tests for Sulphurous Acid and Sulphites.

1. Sulphurous acid, or sulphites from which the acid has been liberated by the previous addition of sulphuric acid, decolorize an acidified solution of potassium permanganate.

2. In the same manner, a solution of potassium bichromate is turned green.

3. Barium chloride in neutral solution gives a white precipitate *soluble in hydrochloric acid.*

4. Paper moistened with mercurous nitrate solution turns black in sulphur dioxide.

Sulphur Trioxide (Sulphuric Anhydride).

Formula, SO_3. Molecular Weight, 80.

This compound is prepared by passing sulphur dioxide and oxygen over heated platinum sponge, or by heating fuming sulphuric acid and condensing the vapors.

In properties, sulphur trioxide forms long, silky, white crystals. It fumes in the air, due to condensation of atmospheric moisture; it has a powerful affinity for water, with which it combines to form sulphuric acid.

Sulphuric Acid, Hydrogen Sulphate (Oil of Vitriol).

Formula, H_2SO_4. Molecular Weight, 98.

This acid is more extensively used in the manufacture of chemical compounds and in the arts than any other one substance, and its manufacture constitutes an important branch of industry.

Sulphuric acid was discovered in the fifteenth century. It was first made by distilling "green vitriol," and for this reason and on account of its oily appearance it was called "oil of

vitriol." The acid is found in nature in combination in the form of sulphates.

Preparation. By passing the fumes of burning sulphur, of nitric acid, steam and air into large leaden chambers, the floor of the chamber being covered with a small quantity of water. These compounds act upon each other with the production of sulphuric acid, which falls to the floor, and is called chamber acid. The simplest expression of the reaction is represented thus:

$$3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO.$$

The nitrogen dioxide takes up oxygen from the air and again assists in forming sulphuric acid:

$$NO + O = NO_2$$
$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO.$$

It is seen from the above that nitric acid and the oxides of nitrogen, in the presence of steam, oxidize sulphurous oxide into sulphuric acid, and that the oxides of nitrogen act as carriers of oxygen from the air.

The chamber acid is drawn off and evaporated in leaden pans to expel water, until the specific gravity is about 1.72. It is further concentrated in glass or platinum vessels to a specific gravity of 1.826, containing 92.5 per cent. of acid.

Properties. Sulphuric acid is a clear, colorless, oily liquid, powerfully corrosive and strongly acid in taste. Its specific gravity is 1.826; boiling point 338°. It has a powerful affinity for water, and removes the latter from the air. In combining with water much heat is set free, and caution must be observed in diluting the acid. It is a powerful acid, displacing all acids more volatile than itself, forming a class of compounds called sulphates. It is very largely used in the arts and in chemical operations. The acid acts on the system as a powerful corrosive poison. *Diluted sulphuric acid* contains 10 per cent. of the pure acid.

Antidotes. Milk of magnesia, chalk, or sodium carbonate, to neutralize the acid, and demulcent drinks to soothe the corroded tissues.

Tests for Sulphuric Acid and Sulphates.

1. Barium chloride gives a white precipitate, insoluble in acids.

2. Solutions of lead salts give a white precipitate of lead sulphate.

3. A solid sulphate fused on charcoal with sodium carbonate, by means of the blowpipe flame, and the resulting mass placed on a bright piece of silver and moistened with hydrochloric acid, gives a black stain.

The impurities which sulphuric acid is liable to contain are lead, nitric acid or nitrogen trioxide, arsenic and selenium. The acid should be completely volatilized at 350°, without residue. The presence of lead is recognized by diluting with water or alcohol, when it precipitates white. Test for nitrates, or nitrogen oxides, by pouring a solution of ferrous sulphate upon some of the acid in a test-tube; a dark color at the line of contact of the two liquids indicates their presence. The gas evolved by mixing the acid with water and pure zinc should not blacken a piece of paper moistened with solution of silver nitrate, showing absence of arsenic. The presence of selenium may be discovered by diluting the acid with water and adding sulphurous acid, when a red color will be formed. Organic matter imparts a dark color to the acid.

Pyrosulphuric Acid, *Fuming sulphuric acid, Nordhausen Oil of Vitriol, Disulphuric acid,* $H_2S_2O_7$. The formula for this acid corresponds to two molecules of sulphuric acid, from which one molecule of water has been withdrawn:

$$2H_2SO_4 - H_2O = H_2S_2O_7.$$

Prepared by distilling anhydrous ferrous sulphate. By dissolving sulphur trioxide in strong sulphuric acid:

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

Properties. A thick, oily, fuming, corrosive liquid. When heated, sulphur trioxide is easily driven off, leaving sulphuric acid.

Test. Pyrosulphates when heated give off sulphur trioxide, leaving the corresponding sulphate.

Thiosulphuric Acid (Hyposulphurous Acid). $H_2S_2O_3$. Not known in the separate state. Found in thiosulphates, chief of which is thiosulphate of sodium. This compound is made by boiling an aqueous solution of sodium sulphite with sulphur, and crystallizing the new compound: its official name is *sodium hyposulphite.*

$$Na_2SO_3 + S = Na_2S_2O_3.$$

Tests for Thiosulphates.

1. Upon adding hydrochloric or sulphuric acid, sulphur dioxide and sulphur are liberated.

2. Silver nitrate produces a white precipitate, which becomes dark on heating.

A list of the other known acids of sulphur is given below. They have no interest except from a scientific standpoint, and some of them are found only in the form of combination in their salts.

Hyposulphurous acid, HSO_2.	Trithionic acid, $H_2S_3O_6$.
Persulphuric acid, $H_2S_2O_8$.	Tetrathionic acid, $H_2S_4O_6$.
Dithionic acid, $H_2S_2O_6$.	Pentathionic acid, $H_2S_5O_6$.

Selenium, $Se'' = 79$; and **Tellurium,** $Te'' = 126$, are both rare elements; the former usually occurs in nature in combination with sulphur, the latter with metals.

The physical properties of selenium are much like those of sulphur, while tellurium has the physical properties of a metal.

Both of these elements form oxides and acids like sulphur. Selenic acid, H_2SeO_4, is distinguished for its power to dissolve gold, a property possessed by no other single acid.

The hydrogen compounds of these elements have an exceedingly offensive and disgusting odor, which fixes itself with tenacity upon the bodies with which it comes in contact.

PHOSPHORUS.

Symbol, P. Atomic Weight, 31. Valence, III.

Occurrence in Nature. Phosphorus does not occur free in nature on account of its great affinity for oxygen. It is found in the form of phosphates widely distributed in all productive soils; as phosphates of calcium, or *apatite,* iron, and aluminum. In some localities the phosphate of calcium is found in large deposits. By the disintegration of minerals containing phosphorus, it is carried into the soil, from which it is absorbed by plants, and from these in turn by animals. In the animal system it is found chiefly in organic combination in the nervous tissues, and in the bones as tricalcium phosphate. It is eliminated chiefly by the urine.

Brand, of Hamburg, first prepared phosphorus in the year 1669, by igniting evaporated urine. Scheele, of Sweden, first succeeded in obtaining it from bones.

Preparation. Bone-ash, or tricalcium phosphate, is digested with two-thirds of its weight of sulphuric acid, thus forming the acid, or superphosphate of calcium in solution:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$

The clear solution is separated from the calcium sulphate by filtration, mixed with charcoal and evaporated to dryness. The residue is heated to expel water and form calcium metaphosphate,

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2H_2O,$$

and further heated to whiteness in retorts of clay, when phosphorus and carbon monoxide are driven off, and calcium pyrophosphate is formed:

$$2Ca(PO_3)_2 + 5C = P_2 + 5CO + Ca_2P_2O_7.$$

The liberated phosphorus is condensed under water. It may be purified by distillation, with exclusion of air.

Properties. The phosphorus obtained by distillation is a colorless, translucent solid, resembling white wax in appearance and consistency. By exposure to light it gradually becomes opaque, and finally turns yellow, acquiring at the same time a coating of reddish-yellow color. At low temperatures it is brittle, but gradually softens under the influence of heat. At the temperature of the air it may be easily cut with a knife. When heated under water it melts at 44.4° C., and volatilizes at 290° when air is excluded. Specific gravity, 1.83 at 10°. Phosphorus is insoluble in water, only slightly soluble in alcohol, ether, the fatty and essential oils. It is freely soluble in bisulphide of carbon and chloroform. Phosphorus unites with oxygen at ordinary temperatures, giving off white fumes which are luminous in the dark, and have the odor of garlic; when exposed, its temperature is soon raised to the point of ignition, and it takes fire spontaneously, burning with a bright, white light and giving off white fumes of phosphoric oxide. It has to be kept under water. Phosphorus takes fire at temperatures slightly above its melting point. On account of its inflammability great caution should be exercised in handling this element. Its burns are severe and difficult to heal, and it should only be handled under water. It combines directly with chlorine, bromine, iodine, sulphur; and with many metals, forming phosphides. The quantivalence of phosphorus is three in some compounds and five in others.

The molecule of phosphorus weighs 124, showing that it contains four atoms.

Phosphorus forms several allotropic modifications. *Amorphous Phosphorus,* prepared by heating phosphorus to a temperature of 260° in an atmosphere of CO_2 for 50 hours.

This form is entirely different from the ordinary variety. It is a reddish-brown, amorphous powder, perfectly inert, and insoluble, and having little affinity for other bodies. Sp. gr.

2.14. Ordinary phosphorus is poisonous; this variety is harmless. It is converted into ordinary phosphorus at 280°.

Metallic Phosphorus is formed by heating phosphorus with lead in a closed tube. On cooling it separates in black, metallic, shining crystals. It is less active than the amorphous variety.

Phosphorus is used in medicine in the free state in the following official preparations: Phosphorated oil, containing one per cent.; Spirit of phosphorus, containing .12 per cent.; Pills of phosphorus, each containing 1/100 grain. It is also used in medicine in the form of its salts, which is a preferable mode of administration.

Phosphorus is largely used in the manufacture of matches. These are usually made by dipping wooden splints in a combustible substance, such as paraffine or sulphur, and then into a paste of phosphorus and potassium chlorate or nitrate.

Poisoning by Phosphorus occurs in two forms, the acute and chronic. Acute poisoning occurs from ingestion of the free element. The symptoms begin with the peculiar garlicky taste of phosphorus in the mouth followed by burning pain in the throat, oesophagus, and abdomen. There is nausea, vomiting, often purging, dilatation of the pupils and great prostration. The extremities become cold, the abdomen is distended, and thirst is intense. In a short time the liver increases in size, and becomes the seat of pain and tenderness. After twenty-four to forty-eight hours symptoms of acute yellow atrophy of the liver supervene, the other symptoms having abated, and if the unfortunate subject survive the acute stage he generally dies of fatty degeneration of the internal organs. The smallest doses known to have destroyed life were 1½ grains in a man and ⅛ grain in a woman.

The antidote for this poison is .5 to 1.0 per cent. solution of potassium permanganate, which should be employed in large quantities to wash out the stomach, and some of it should be allowed to remain in the stomach for absorption.

Chronic poisoning may result from the long continued administration of phosphorus in large doses, or from exposure to phosphorus fumes such as occurs in match factories. The symptoms are great weakness, loss of appetite, abdominal pain, sallow complexion, necrosis of the lower jaw, if the teeth are carious, with swelling and suppuration of the gums.

The treatment consists in withdrawing the poison and repairing the teeth.

COMPOUNDS OF PHOSPHORUS WITH HYDROGEN.

Hydrogen Phosphide, *Phosphoretted Hydrogen, Phosphine,* PH_3. Prepared by boiling phosphorus with solution of potassium, or sodium hydroxide, or milk of lime. Phosphine prepared in this way is spontaneously inflammable, due to the presence of a liquid volatile compound of the composition P_2H_4, which is highly inflammable; this compound deposits on standing in sunlight a third phosphide of hydrogen, P_4H_2, which is a yellow solid.

Properties. Phosphine is a colorless gas, having the odor of garlic. It is a powerful poison when inhaled, acting as a reducing agent upon the blood, and preventing further absorption of oxygen. Hydrogen phosphide is formed during the decomposition of organic bodies containing phosphorus, in the presence of water; upon coming in contact with the air it takes fire spontaneously, producing the "Will o' the wisp," or *ignis fatuus,* so often seen in marshes.

Phosphine resembles ammonia in some of its chemical relations, having a similar composition—NH_3, PH_3—but is much less basic. It unites with the halogen acids with retention of hydrogen, forming compounds like the ammonium salts:

$$PH_4Cl - PH_4Br - PH_4I.$$

The basic radical in these compounds is called *Phosphonium.*

COMPOUNDS OF PHOSPHORUS WITH OXYGEN.

Phosphorus forms two well-known oxides:

P_2O_3, Trioxide, or Phosphorous Oxide; and

P_2O_5, Pentoxide, or Phosphoric Oxide.

Phosphorous Oxide is formed by the slow oxidation of

phosphorus in air, as a white powder, having strong affinity for water. By combination with water it produces phosphorous acid:

$$P_2O_3 + 3H_2O = 2H_3PO_3.$$

Phosphoric Oxide, Phosphoric Anhydride. Prepared by burning phosphorus in an abundant supply of air; is a snow white powder. By exposure to moist air it deliquesces to a liquid, and, when thrown into water, combines with the latter with explosive violence. Its affinity for water is greater than that of sulphuric anhydride. Phosphoric oxide combines with water in three different proportions, forming three distinct phosphoric acids:

$$P_2O_5 + H_2O = 2HPO_3, \text{ Metaphosphoric acid.}$$

$$P_2O_5 + 2H_2O = H_4P_2O_7, \text{ Pyrophosphoric acid.}$$

$$P_2O_5 + 3H_2O = 2H_3PO_4, \text{ Orthophosphoric acid.}$$

Hypophosphorous Acid, H_3PO_2, H,H_2PO_2. This acid has no corresponding oxide.

Preparation. By heating the hydroxide of sodium, of potassium, or of calcium with water and yellow phosphorus, the hypophosphite of these bases is formed in solution, and hydrogen phosphide escapes:

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

$$8P + 3Ca2OH + 6H_2O = 3Ca2H_2PO_2 + 2PH_3.$$

When oxalic acid is added to the solution of calcium hypophosphite, calcium oxalate precipitates, and hypophosphorous acid remains in solution. The acid may be separated by filtration, and reduced to a syrupy consistence by evaporation.

Properties. Hypophosphorous acid is a colorless, thick syrupy liquid, strongly acid in reaction. At a temperature below 0°, it is a white, crystalline solid. It has strong affinity for oxygen and acts as a powerful reducing agent, becoming

converted into phosphoric acid. It is soluble in water. A 30 per cent. solution is official in the U. S. P. as hypophosphorous acid, and a 10 per cent. solution is official also as diluted hypophosphorous acid. It forms a class of salts known as hypophosphites. Though containing three hydrogen atoms, it is a monobasic acid, only one of these being replaceable by metals.

Tests for Hypophosphorous Acid and Hypophosphites.

1. When heated in the solid state they take fire, with elimination of PH_3, leaving the pyrophosphate.

2. They give a white precipitate with silver nitrate which turns brown on heating.

3. When mixed with a solution of mercuric chloride, and a few drops of HCl, a white precipitate slowly forms.

4. They decolorize an acid solution of potassium permanganate.

Phosphorous Acid, H_3PO_3, H_2HPO_3.

Preparation. By dissolving phosphorus oxide in water:

$$P_2O_3 + 3H_2O = 2H_3PO_3.$$

Properties. When the solution is evaporated under the receiver of an air pump it forms crystals of pure phosphorous acid, which are deliquescent and very soluble in water. The acid is generally seen as a clear, colorless liquid, which absorbs oxygen and becomes converted into phosphoric acid. It is a powerful reducing agent. Phosphorous acid forms a class of compounds called phosphites. It is a dibasic acid, and forms normal and acid salts, according to the number of hydrogen atoms replaced.

Tests for Phosphorous Acid and Phosphites.

1. They give white precipitates with barium chloride, and lead acetate. Hypophosphites do not.

2. They give a precipitate of calomel with mercuric chloride solution.

3. With silver nitrate a black precipitate of metallic silver.

Phosphoric Acid, *Orthophosphoric Acid.* Common or ordinary phosphoric acid, H_3PO_4. Occurs in nature in form of phosphates.

Preparation. When phosphoric oxide is dissolved in hot water this acid is produced. Usually made by gently heating yellow phosphorus with diluted nitric acid.

$$5HNO_3 + 3P + 2H_2O = 3H_3PO_4 + 5NO.$$

The liquid is heated until fumes of nitrogen dioxide, and any excess of nitric acid are driven off.

Properties. A colorless acid liquid, containing 85 per cent. of H_3PO_4, and having a specific gravity of 1.707. Phosphoric acid is a tribasic acid, forming salts known as phosphates, of which there are three classes, according to the number of hydrogen atoms replaced in each case. The composition of these compounds is explained in the following equations:

Na_3PO_4, Normal, or trisodium phosphate.

Na_2HPO_4, Disodium hydrogen phosphate.

NaH_2PO_4, Sodium dihydrogen phosphate.

Also known as primary, secondary, and tertiary phosphates of sodium.

The anhydrous acid forms colorless, prismatic crystals.

The diluted phosphoric acid of the U. S. P. contains 10 per cent. of the absolute acid.

Tests for Phosphoric Acid and Phosphates.

1. The salts of phosphoric acid give white precipitates with barium or calcium chloride, soluble in acetic and mineral acids.

2. Silver nitrate gives a lemon yellow precipitate, soluble in nitric acid or ammonium hydroxide.

3. With magnesium sulphate, ammonium chloride, and ammonium hydroxide a white precipitate forms; soluble in acids.

4. With solution of ammonium molybdate in nitric acid, a yellow precipitate forms; soluble in ammonium hydroxide.

5. Solution of egg albumen is not precipitated by the acid or its salts when acidified by acetic acid.

Pyrophosphoric Acid, $H_4P_2O_7$. *Prepared* by continuously heating orthophosphoric acid at a temperature of 250°. Sodium pyrophosphate may be easily prepared by heating the disodium hydrogen phosphate.

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$
$$2H_3PO_4 \quad = H_4P_2O_7 \; + H_2O.$$

Properties. A white, crystalline solid, soluble in water, and when in solution gradually changes to orthophosphoric acid. It forms pyrophosphates, and is tetrabasic. Solutions of pyrophosphates give a white precipitate with silver nitrate.

Metaphosphoric Acid, HPO_3. *Prepared* by heating orthophosphoric acid to a temperature of 400°,

$$2H_3PO_4 = 2H_2O + 2HPO_3,$$

also formed by dissolving phosphoric oxide in cold water,

$$P_2O_5 + H_2O = 2HPO_3.$$

Properties. A transparent, glassy mass. Sometimes called "glacial phosphoric acid." Deliquescent and freely soluble in water. It forms salts called metaphosphates, and is monobasic. The acid has the power of coagulating albumen, by which means it may be distinguished from pyrophosphoric acid. Its salts give a white precipitate with silver nitrate in neutral solution, but no precipitate with magnesium sulphate, ammonium chloride, and hydroxide.

THE HALOGENS.

The elements fluorine, chlorine, bromine, and iodine, show great resemblance in properties; their chemical properties being

almost identical. They are termed *halogens,* or *salt producers,* because they form salts by direct combination with other elements. The compound radical, cyanogen (CN), was formerly classed as a member of this group.

The halogens show a direct relation between properties and atomic weights, showing a gradation in properties with increase of specific gravity of the elements in the state of gas. Fluorine, with an atomic weight of 19, is a gas, and possesses the strongest chemical affinities of all known substances. Chlorine, whose atomic weight is 35.4, is a less tenuous gas, and its chemical affinities are not so strong as those of fluorine; bromine, having an atomic weight of 79.8, is a volatile liquid, whose chemical affinities are less active than those of chlorine; and iodine, with an atomic weight of 127, is a solid and the least active. They are all univalent.

CHLORINE.

Symbol, Cl. Atomic Weight, 35. Valence, I.

Chlorine was discovered by Scheele, of Sweden, in 1774, and its elementary character was first established by Gay Lussac.

Occurrence in Nature. On account of the readiness with which chlorine combines with other elements, it is not found in the free state. It is found in the form of chlorides of the metals, potassium, magnesium and calcium, and most abundantly as the chloride of sodium in deposits in the earth, and dissolved in sea water.

Preparation. By gently heating the black oxide of manganese and hydrochloric acid in a retort chlorine is given off as a gas, which may be collected over warm water, or by displacement of air.

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2.$$

It may also be prepared by the oxidizing action of potassium chlorate, bichromate, or permanganate, chromic or nitric acids

upon hydrochloric acid, whereby the hydrogen is converted into water and chlorine is set free.

By heating together manganese dioxide, sodium chloride and sulphuric acid according to the equation:

$$MnO_2 + 2NaCl + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + Cl_2.$$

Properties. A yellowish-green gas, of penetrating, suffocating odor, producing irritation and inflammation of the air passages when inhaled. Its specific gravity compared with hydrogen is 35.45; with air, 2.45. At a pressure of about six atmospheres, or a temperature of 40°, it forms a yellow liquid. One volume of water absorbs about two volumes of the gas at ordinary temperatures. When a saturated solution of chlorine in water is cooled below 0°, yellow, scaly crystals of chlorine hydrate (Cl_2 $10H_2O$) separate.

Chemically, chlorine is a most active element. It combines directly with all elements except oxygen, carbon, and nitrogen, and it may be made to unite with these indirectly. Finely divided arsenic, antimony, or copper will take fire when thrown into chlorine; phosphorus takes fire spontaneously in the gas. Its affinity for hydrogen is so great that it often removes this element from combination with other bodies. A mixture of hydrogen and chlorine may be kept in the dark without combination taking place, but when such a mixture is exposed to diffused light, the two gradually unite; when exposed to sunlight, or to the influence of the electric spark, combination takes place with explosive violence. It decomposes hydrocarbons and ammonia with removal of their hydrogen. A candle burns in the gas with a smoky flame. Chlorine, in the presence of moisture, acts as a powerful bleaching and disinfecting agent, either by direct combination with the substance, or by uniting with the hydrogen of water and setting oxygen free, the liberated oxygen acting very energetically in the nascent state. It forms chlorides by union with other elements.

Experiment. Place a small quantity of black oxide of manganese in a dry test-tube, add enough hydrochloric acid to cover the oxide, shake well and heat gently. Collect the gas in a test-tube by downward displacement and cover the receiving vessel with a piece of moistened cardboard. Observe the properties of the gas as described above.

Chlorine Water is "an aqueous solution, containing, when freshly prepared, about 0.4 per cent. of chlorine, with some of the oxides of chlorine and potassium chloride"—U. S. P., 1900. It is made by placing potassium chlorate in a flask and adding hydrochloric acid. Cold water is then added in small portions at a time so as to dissolve the escaping gases. Chlorine water is a greenish-yellow liquid, having many of the properties of chlorine. By exposure to light it is gradually decomposed into hydrochloric acid and oxygen.

Hydrogen Chloride, Hydrochloric Acid, Muriatic Acid, Spirit of Salt.

Formula, HCl. Molecular Weight, 36.4.

The elements hydrogen and chlorine enter into direct combination in the proportion of volume for volume, with the production of hydrochloric acid. This union takes place, when the two gases are mixed, under the influence of the flame, the electric spark or light.

Preparation. Hydrochloric acid may be prepared by heating a mixture of sodium chloride, or other chloride, with sulphuric acid and collecting the vapors of hydrochloric acid, which are thereby evolved. It is also formed as a by-product in the manufacture of sodium carbonate by the Leblanc method:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Properties. A colorless gas, with a suffocating and penetrating odor, producing great irritation to the air passages. The gaseous acid may be liquefied by a pressure of 40 atmospheres at a temperature of about 15°. It is not combustible nor a supporter of combustion, and is very soluble in water. One volume of water at 0° will dissolve about 500 volumes of the gas; at ordinary temperatures about 400 volumes. On account

of its great affinity for water the gas forms white clouds of liquid hydrochloric acid in moist air.

The hydrochloric acid of commerce and of the arts is a solution of the above-described gas in water, and constitutes a very important preparation. The acid of the U. S. P. consists of 31.9 per cent. of pure HCl dissolved in water, and has a specific gravity of 1.158. It is a transparent colorless liquid, strongly acid in taste and reaction, and very corrosive; giving off white fumes when exposed to the air.

A distinct hydrate may be formed by passing pure dry hydrogen chloride into the concentrated aqueous solution, cooled to a temperature of — 22°. The hydrate separates in the form of crystals, having the formula $HCl.2H_2O$.

A mixture of hydrochloric acid and snow acts as a powerful refrigerant, reducing the temperature to — 32°.

The diluted hydrochloric acid of the U. S. P. contains 10 per cent. of pure HCl.

Hydrochloric acid is univalent acid, forming salts known as chlorides.

Tests for Hydrochloric Acid and Chlorides.

1. A glass rod moistened with solution of ammonia brought in the presence of the free acid gives dense white fumes of ammonium chloride.

2. Solution of mercurous nitrate when added to a chloride gives a white precipitate of calomel, which blackens with ammonia water.

3. Silver nitrate added to solution of a chloride gives a white curdy precipitate, insoluble in nitric acid, soluble in ammonia water.

4. When heated with manganese dioxide and sulphuric acid they give off chlorine.

5. In strong solution they give a white precipitate with lead acetate, which is soluble in hot water.

Nitro-hydrochloric Acid, *Nitro-muriatic Acid* (*Aqua Regia*). This substance is not a definite chemical compound, but is made by mixing nitric and hydrochloric acids, and contains free chlorine, chloronitrous (NOCl) and chloronitric ($NOCl_2$) gases.

By mixing 180 c.c. of nitric acid with 820 c.c. of hydrochloric acid, and allowing the mixture to stand in an open vessel until effervescence ceases, this acid is obtained.

Properties. A yellow, fuming, corrosive liquid; capable of dissolving gold and platinum, on account of the presence of the free chlorine, and chloronitrous and chloronitric gases, forming the chlorides of these metals.

Diluted nitro-hydrochloric acid is made by mixing 40 c.c. nitric acid with 182 c.c. hydrochloric acid, and, when effervescence has ceased, adding 780 c.c. of distilled water.

THE OXIDES AND OXYGEN ACIDS OF CHLORINE.

Though chlorine and oxygen do not enter into direct union, yet compounds of these elements are made by indirect means. The following oxides and acids are known:

Chlorine monoxide, hypochlorous oxide, Cl_2O.
Chlorine peroxide, or dioxide, ClO_2.
Hypochlorous acid, HClO.
Chlorous acid, $HClO_2$.
Chloric acid, $HClO_3$.
Perchloric acid, $HClO_4$.

Hypochlorous Oxide and Acid, Cl_2O and HClO. Hypochlorous oxide is *prepared* by passing dry chlorine over dry mercuric oxide, and condensing the gas in a cooled glass tube:

$$HgO + 2Cl_2 = Cl_2O + HgCl_2.$$

Properties. A reddish-brown liquid below 5°; above that temperature a yellowish gas, which easily decomposes with explosive violence.

Hypochlorous acid is only known in aqueous solution, and can be made by passing chlorine into water containing freshly precipitated mercuric oxide. It may be concentrated by careful distillation, and has a yellow color, sweetish taste, and strong, bleaching properties. It is very unstable.

This acid forms an important class of salts called hypochlorites, which are most conveniently prepared by the action of chlorine upon alkaline hydroxides at the ordinary temperature of the air.

$$2NaOH + Cl_2 = NaCl + H_2O + NaClO.$$

Chlorous acid is of scientific interest only.

Chloric Acid, $HClO_3$, on account of its salts, is the most important oxygen acid of chlorine.

Preparation. By the action of sulphuric acid upon an aqueous solution of barium chlorate, separating the clear liquid from the precipitate, and concentrating under an air-pump to a specific gravity of 1.28.

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

Properties. An oily, acid liquid which decomposes at 40°. A powerful oxidizing agent, capable of inflaming alcohol and sulphur. It forms a class of salts denominated chlorates.

Chlorates are generally prepared by the action of chlorine upon the *hot* aqueous solution of the alkalies:

$$6NaOH + 3Cl_2 = 5NaCl + 3H_2O + NaClO_3.$$

Perchloric Acid, $HClO_4$. *Preparation.* By heating potassium chlorate, oxygen is driven off and perchlorate of potassium remains.

$$2KClO_3 = KCl + KClO_4 + O_2.$$

By mixing sulphuric acid with the potassium perchlorate, and distilling, perchloric acid is obtained:

$$2KClO_4 + H_2SO_4 = K_2SO_4 + 2HClO_4.$$

Properties. A colorless, fuming, corrosive, mobile liquid; specific gravity, 1.78. When kept for a few days it decomposes with violent explosion. Explodes when brought in contact with organic substances. Forms perchlorates by combination with bases.

Tests for Chlorates.

1. They deflagrate when heated on charcoal.
2. They give up oxygen when strongly heated.

Hypochlorites evolve chlorine upon the addition of an acid, and may be recognized by this and their bleaching properties.

Chlorine Dioxide, Chlorine Peroxide, ClO_2, is formed by the action of sulphuric acid upon potassium chlorate in the cold.

Properties. It is a gas, having a deep yellow color and powerful odor. By cold it can be condensed to a reddish-brown liquid. Both the liquid and gaseous chlorine dioxide are violently explosive. On account of the formation of this compound, sulphuric acid should not be added to potassium chlorate without great caution.

BROMINE.

Symbol, Br. Atomic Weight, 79. Valence, I.

History and Occurrence in Nature. Discovered by Balard in 1826. Found in small quantities in sea water and mineral waters, as magnesium and sodium bromide.

Preparation. When sea water is evaporated the sodium chloride first crystallizes, and the mother-liquor contains magnesium and sodium bromide. The mother-liquor is treated with chlorine, which forms the chloride of the bases present, with liberation of bromine. Bromine thus liberated is separated by distillation and condensed in a cooled receiver:

$$2NaBr + Cl_2 = 2NaCl + Br_2.$$

Properties. Bromine is a thin, dark, reddish-brown liquid, and when exposed to the air gives off yellowish-red fumes,

which have a disagreeable suffocating odor and irritant action on the air passages. It boils at 63° and solidifies at —7° into a yellow-green scaly mass, having a metallic appearance resembling iodine. Its specific gravity is 2.99. It is soluble in thirty parts of water, and when the aqueous solution is cooled below 4°, crystals of bromine hydrate ($Br_2.10H_2O$) separate. It is soluble in alcohol, more soluble in ether, chloroform and bi-sulphide of carbon. In its chemical properties bromine shows great resemblance to chlorine, like that element, combining directly with most metals, with formation of bromides. It differs from chlorine in the fact that its chemical affinities are weaker, and is displaced from its compounds by chlorine. It unites with hydrogen under the influence of heat, forming hydrobromic acid. It acts as a disinfectant and bleaching agent in the presence of water.

Hydrobromic Acid, HBr.

Preparation. By warming a solution of potassium bromide and dilute sulphuric acid, and separating the hydrobromic acid by distillation:

$$2KBr + H_2SO_4 + xH_2O = K_2SO_4 + xH_2O + 2HBr.$$

If strong sulphuric acid is added to a bromide the bromine is set free.

The acid may be prepared in solution by passing hydrogen sulphide through bromine under water until the color of bromine disappears:

$$2H_2S + 4H_2O + 10Br = H_2SO_4 + S + 10HBr.$$

The acid is then separated by filtration and distillation.

Properties. A colorless gas, having a pungent odor, an acid taste and reaction, freely soluble in water, imparting its acid properties to the latter.

Diluted hydrobromic acid of the U. S. P. contains 10 per

cent. HBr, and has a specific gravity of 1.076. It is a colorless acid liquid.

Hydrobromic acid by combination with bases forms bromides.

Tests for Bromides.

1. When a crystal of bromide is dropped in a solution of cupric sulphate acidified with sulphuric acid, a reddish-brown color is produced, due to the formation of cupric bromide.

2. They give with solution of silver nitrate a light-yellow precipitate of silver bromide, insoluble in nitric acid, slightly soluble in ammonia water.

3. Nitric acid, or chlorine added to solution of a bromide liberates bromine, which may be removed by shaking with ether.

4. Free bromine imparts an orange color to mucilage of starch.

5. Strong sulphuric acid dropped upon a dry bromide liberates reddish vapors of bromine.

The oxygen acids of bromine are:

$HBrO$, Hypobromous Acid,
$HBrO_3$, Bromic Acid,
$HBrO_4$, Perbromic Acid.

These acids and their compounds are similar in method of preparation and properties to the corresponding compounds of chlorine.

No oxides of bromine have ever been obtained.

IODINE.

Symbol, I. Atomic Weight, 126. Valence, I.

Occurrence in Nature. Iodine occurs in combination as sodium, potassium, or magnesium iodide. In these forms it occurs in small quantity in certain mineral springs (Austria and Bavaria) and in sea water. The salts of iodine are absorbed

by sea weeds, and the iodine is largely obtained from the ash of these plants.

Preparation. Kelp, or the ash of sea weeds, is washed with water in order to remove its soluble constituents; the resulting liquid is evaporated to concentration and allowed to cool, when the chlorides and carbonate of sodium and potassium are removed by crystallization. The remaining mother-liquor is heated in a retort with the black oxide of manganese and sulphuric acid, and the liberated iodine is condensed in a cooled receiver.

$$MnO_2 + 2H_2SO_4 + 2NaI = Na_2SO_4 + MnSO_4 + 2H_2O + I_2.$$

Iodine may also be liberated from its compounds by passing chlorine through solutions containing them. It is now prepared from the mother-liquor of Chili saltpeter, where it exists as the iodate.

Properties. Iodine is a dark, bluish-black solid, forming crystalline scales, which have a distinct metallic lustre. It gives off a peculiar odor, resembling that of chlorine, stains the skin brown, and is corrosive to a less extent than bromine. Its specific gravity is 4.95; it fuses at a temperature of 114°, and boils at 180°. The vapor of iodine has a beautiful violet color. It volatilizes slowly at ordinary temperatures when exposed to the air. Iodine is only slightly soluble in water, about one in 5,000 to 7,000 parts; the aqueous solution has a reddish-brown color. The solubility of iodine in water is greatly increased by the presence of the iodides of the alkalies, or hydriodic acid.

It is soluble in about ten parts of alcohol—tincture of iodine—more soluble in ether, chloroform, and carbon bisulphide. In chemical properties iodine resembles chlorine and bromine, differing from these elements in the intensity of its affinities, which are much weaker; on this account it is liberated from combination by these elements.

Iodine is largely used in medicine, both in the elementary state and in combination. It acts as a corrosive irritant poison when the dose is excessive, and mucilage of starch is used as an antidote.

Hydrogen Iodide, Hydriodic Acid, HI.

Preparation. A glass tube is selected, a few fragments of phosphorus are placed in the bottom, then a layer of broken glass, then a layer of iodine. The tube is filled in this manner, with alternating layers of phosphorus, glass, and iodine, the glass being moistened with water. When gentle heat is applied, vapors of hydriodic acid escape, and may be collected by displacement of air through a delivery tube. The phosphorus and iodine combine, and in the presence of water form hydriodic acid:

$$PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

Hydriodic acid may be obtained in solution by the action of hydrogen sulphide upon iodine in the presence of water:

$$I_2 + H_2S + xH_2O = S + 2HI + xH_2O.$$

Properties. A colorless gas, having an irritating, suffocating odor, forms white fumes in the air. It is analogous in properties to the corresponding compound of chlorine. Liquefied by pressure of 4 atmospheres at 0°; solidifies at — 55°. Soluble in water; one volume taking up 427 volumes, imparting acid properties. Its aqueous solution undergoes decomposition by oxidation of the hydrogen, when the iodine is set free and dissolves, imparting a brown color.

Diluted hydriodic acid, U. S. P., contains "not less than 10 per cent., by weight, of the absolute acid."

Tests for Hydriodic Acid and Iodides.

1. They give a blue color with mucilage of starch and chlorine water.

2. To solution of iodide add chlorine water and shake with chloroform; the chloroform separates as a violet-colored layer.

3. They give a pale-yellow precipitate with solution of silver nitrate; practically insoluble in diluted nitric acid, and ammonia water.

4. They give a yellow precipitate with solution of lead acetate.

5. They give a yellow precipitate, which turns red, with solution of $HgCl_2$.

6. Dry iodide with sulphuric acid gives vapors of iodine.

The oxygen acids of iodine are:

HIO_3 — Iodic Acid.

HIO_4 — Periodic Acid.

Iodic acid is formed by dissolving iodine in strong nitric acid, evaporating to dryness and heating to redness, and dissolving the resulting oxide of iodine I_2O_5 in water. It is a white crystalline soluble solid.

These acids are analogous to the corresponding acids of chlorine, and their salts are prepared in the same way.

FLUORINE.

Symbol, F. Atomic Weight, 19. Valence, I.

On account of its intense chemical activity it is extremely difficult to keep fluorine in the elementary state long enough to examine its properties. It was obtained free by Moissan in 1887.

Occurrence in Nature. Fluorine is found as the fluoride of calcium, CaF_2, in minerals; in small quantity as a constituent of bones, and the enamel of teeth.

Preparation. By electrolysis of hydrogen fluoride in vessels of platinum at a temperature of about $-23°$, the element is obtained in a free state.

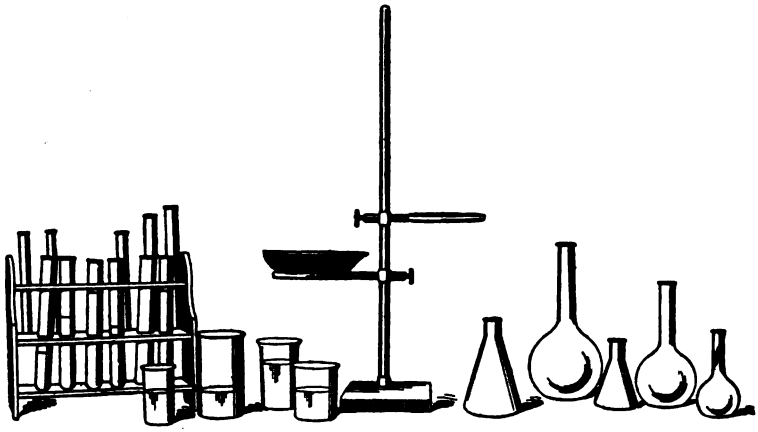
Properties. A greenish-yellow, tenuous gas; having a dis-

agreeable and very irritating odor, producing inflammation of the air passages when inhaled, even in small quantity.

It has a powerful affinity for nearly all the other elements, uniting with hydrogen with great violence, even at low temperatures, and combining with carbon, sulphur, phosphorus, boron, silicon, arsenic and calcium with production of flame. It combines with iron with incandescence, and attacks silver, lead and mercury. It decomposes water with production of hydrofluoric acid and liberation of ozone, in fact, it is the most active of the elements.

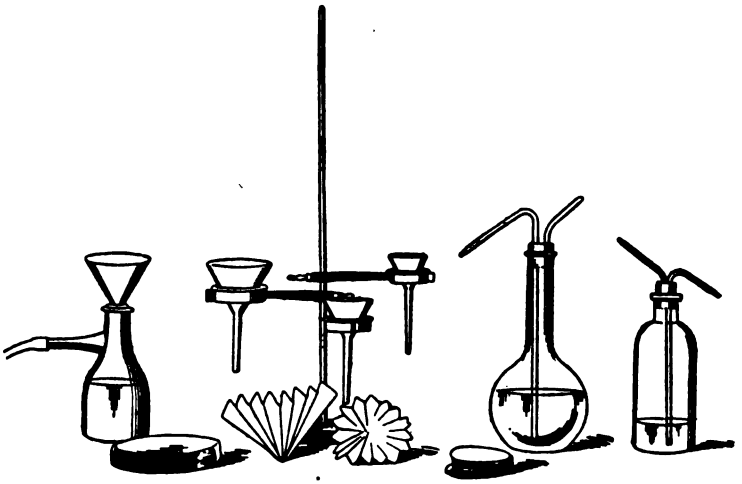
Hydrofluoric Acid, *Hydrogen fluoride,* HF. *Prepared* by distilling calcium fluoride and sulphuric acid in platinum or leaden vessels. In *properties,* it is a colorless, extremely volatile, fuming, corrosive liquid. Its boiling point is 19°, specific gravity .98 at 12°. In order to recondense the gas it must be cooled to — 20°. It attacks glass and porcelain energetically and most metals; therefore, it has to be kept in vessels of caoutchouc. When dropped upon the skin it produces painful and indolent ulcers. It is used for etching glass.

FIG. 35.



Apparatus for Solution.—Test Tubes, Beakers, Retort Stand, Flasks.
(After Rockwood.)

FIG. 36.



Apparatus for Filtration. (After Rockwood.)

THE METALLIC ELEMENTS.

General Properties. Only about one-half of the total number of fifty-eight metallic elements are of sufficient importance to engage our attention. Many of them are exceedingly rare and are of interest only to the student of theoretical chemistry.

The physical properties of the metals furnish their chief distinguishing characteristics. They have a peculiar appearance known as *metallic lustre* due to their high degree of opacity and great power to reflect light. A smooth surface, however, is necessary to produce the lustrous appearance, and for this reason they generally appear as a black deposit when precipitated in a finely divided state. The most lustrous metals, such as gold and silver, lose this property when precipitated from solution in fine powder.

The metals are good conductors of heat and electricity; they present the properties of malleability, ductility and hardness to varying degrees; they are generally fusible, and many of them can be volatilized. The specific gravities present a wide range, varying from .59 for lithium to 22.4 for osmium.

Most of the metals have a gray or bluish-gray appearance, few of them having any decided color. Those showing a distinct color are copper, which is red; and calcium, barium and gold, which show different shades of yellow. Silver is pure white.

The metals form many compounds with non-metals by direct union, most of them uniting with phosphorus, sulphur, chlorine, bromine, iodine and oxygen. The oxides are usually basic in character, which distinguishes them strongly from the non-metals whose oxides are acidic. There are some few metals, however, which form acid oxides since there is no abrupt line of demarkation between metals and non-metals.

Alloys. Metals show little tendency to combine among

themselves, though in some cases it is probable that a chemical compound is formed by fusing them together. An alloy is made by fusing two or more metals together, and it is believed to be partly a chemical compound and partly a mechanical mixture. In the alloy, we find the metallic character retained and about the average of the properties of its constituents; the fusing point and conductivity are reduced below the mean.

Amalgams are alloys in which one of the constituents is mercury.

Preparation of Metals. A great many of the metals occur in nature in the form of sulphide, oxide or carbonate, and on this account we can form general rules for their preparation. In order to prepare a metal from an ore in which it occurs as sulphide, the sulphide is roasted, or heated in air, thus forming the oxide and the oxide is then heated with carbon, thus liberating the metal. Let R stand for any metal, and the following equation will represent the changes taking place:

$$RS + O_3 = RO + SO_2,$$

$$RO + C = CO + R.$$

When the metal occurs in nature as oxide or carbonate it is prepared by heating with carbon, thus:

$$RCO_3 + C_2 = R + 3CO.$$

Classification of the Metals.

The metals may be classified in many different ways but the simplest and most convenient is based chiefly upon their analytical reactions, as follows:

Light Metals. In these the specific gravity is from .6 to 6; and the sulphides are soluble.

Heavy Metals. In these the specific gravity is from 6 to 22; and the sulphides are insoluble.

The metals are further subdivided into groups, thus:

Alkali metals.	Alkaline earth metals.
K, Na, NH_4, Li, Cs, Rb.	Ba, Ca, Sr, Mg.
Earth metals.	Iron group.
Al, and certain rare metals.	Fe, Co, Ni, Mn, Cr, Zn.
Lead group.	Arsenic group.
Pb, Cu, Bi, Ag, Hg, Cd.	As, Sb, Sn, Au, Pt, Mo.

The noble metals are mercury, silver, gold, platinum, palladium, rhodium, ruthenium, osmium, and iridium. These metals may be separated from their oxides (when oxides are formed) by simply heating to redness.

ALKALI METALS.

The metals *potassium* (*rubidium, caesium*), *lithium, sodium,* and the compound *ammonium* constitute the members of this group. They are decidedly the most basic of the metals in their character, and have been grouped together on account of great similarity in physical and chemical properties, both in the elementary state and in their compounds.

They are silvery white metals, capable of fusion at a moderate temperature. When exposed to the air they quickly oxidize; they decompose water at all temperatures, forming hydroxides, which dissolve to form an alkaline solution; for this reason called alkali metals. Their chemical affinities increase with increasing atomic weight. They form soluble oxides, hydroxides, carbonates, phosphates, sulphides, nitrates and halogen salts. They are the only metals whose hydroxides and carbonates are not decomposed by heat. Their hydroxides are known as *caustic alkalies*. They are all univalent.

POTASSIUM (Kalium).

Symbol, K. Atomic Weight, 39. Valence, I.

Potassium was discovered by Sir Humphrey Davy in 1807, who obtained it by electrolysis of the moistened hydroxide.

Occurrences in Nature. This element is found in nature as the chloride and sulphate in large deposits in Stassfurt, and as the nitrate in some soils in hot countries. It occurs in these forms in certain mineral waters, and to some extent in sea water. It is found also as the double silicate of potassium and aluminum in granite rocks and feldspar. By the gradual disintegration of these rocks the potassium is rendered soluble, and is carried into the soil, from which it is absorbed by growing plants. In the tissues of plants it exists in combination with organic acids, as the tartrate, citrate, etc. When plants are burned the potassium present is converted into carbonate, and remains in the ash. By washing the ash of plants with water —or lixiviating—filtering and evaporating the solution to dryness, an impure potassium carbonate is obtained, known as *crude potash.* When crude potash is heated to redness, to expel organic matter, it is called *pearlash.* This salt was for a long time the source of all the compounds of potassium, but they are now chiefly prepared from the chloride, which is found in great abundance in nature.

Preparation. Metallic potassium is obtained by heating the carbonate with carbon in iron retorts, condensing the volatilized metal in flat-shaped iron receivers, and cooling in rectified petroleum. The chemical changes taking place are shown in the equation:

$$K_2CO_3 + C_2 = 3CO + K_2.$$

The distillation of potassium has to be conducted with a great deal of care on account of the formation of an explosive compound of the metal with carbon monoxide. It is also prepared by electrolysis of the fused hydroxide.

Properties. A silvery-white solid, having a bright metallic lustre; soft enough to be easily cut with a knife. Its specific gravity is .86; fusing point 62.5°. At a red heat it volatilizes to a greenish vapor, when air is excluded, but when heated in the air it burns with a violet-colored flame, forming the oxide.

Potassium when exposed to the air becomes rapidly tarnished on account of its affinity for oxygen, and soon acquires a coating of hydroxide by the simultaneous action of atmospheric moisture; therefore, in order to preserve it, it must be kept in a liquid destitute of oxygen, or in an atmosphere of hydrogen. It decomposes water with formation of the hydroxide and liberation of hydrogen, the chemical action being so intense as to cause the latter to take fire at the moment of liberation.

It combines directly and energetically with the halogens.

COMPOUNDS OF POTASSIUM.

Potassium Oxide, or **Monoxide,** K_2O. Formed by oxidation of thin sheets of the metal in dry air, or by heating the hydroxide with potassium:

$$2KOH + K_2 = 2K_2O + H_2.$$

Properties. A white powder, having great affinity for water to form the hydroxide. Capable of fusion, and of being volatilized at a high temperature. The *peroxide,* K_2O_2, and *tetroxide,* K_2O_4, are known.

Potassium Hydroxide, *Caustic Potash,* KOH. *Preparation.* By the action of the monoxide on water. By boiling a solution of potassium carbonate with calcium hydroxide:

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3.$$

The supernatant liquid is separated from the precipitated calcium carbonate by decantation, heated until water is expelled and allowed to solidify.

Properties. A hard, white, crystalline mass, very deliquescent, and soluble in four-tenths parts water, two parts alcohol. It melts to an oily liquid when heated, and may be poured into moulds to form pencils. At a red heat it volatilizes without decomposition. Caustic potash is a powerful base; destroys

organic matter, and combines with acids to form salts. It acts as a corrosive poison, dissolving the tissues and saponifying fats. Weak acids and oils are used as antidotes. The liquor potassæ of the U. S. P. is a 5 per cent. aqueous solution of potassium hydroxide.

The compounds of potassium with the halogens may be obtained by direct union of the elements, or by the action of halogen acids upon potassium hydroxide. They form cubical crystals, freely soluble in water, having a salty taste, and capable of fusion and volatilization by heat.

Potassium Chloride, KCl, occurs abundantly in nature in an impure state in sea water, in mineral springs, and in the salt mines of Stassfurt, Germany. *Prepared* by recrystallization of the salt found in nature, or by neutralizing hydrochloric acid with potassium carbonate:

$$2HCl + K_2CO_3 = 2KCl + H_2O + CO_2.$$

Properties. White cubical crystals. Soluble in three parts water, insoluble in alcohol. When heated the salt melts, and at a red heat it volatilizes. It is largely used for preparing other potassium compounds.

Potassium Iodide, KI. *Prepared* by dissolving iodine in solution of potassium hydroxide in sufficient quantity to form a permanent yellowish color. This forms a solution of the iodide and iodate of potassium, according to this equation:

$$6KOH + 6I = 5KI + KIO_3 + 3H_2O.$$

The liquid is then evaporated to syrupy consistency and mixed with wood charcoal, dried and heated to redness, when the iodate is converted into iodide, as shown by the equation:

$$KIO_3 + 3C = KI + 3CO.$$

The residue is next washed with water, filtered and evaporated for the formation of crystals.

Properties. White, opaque, cubical crystals, or a white, granular powder; saline taste, faintly alkaline reaction. Crystals white when obtained from alkaline solution, transparent when obtained from neutral solution. Soluble in .7 parts water, .5 parts boiling water, 12 parts alcohol, and 2.5 parts glycerine. The salt when exposed to the air assumes a slightly yellowish color from liberation of iodine. It should not give a blue color with mucilage of starch, showing absence of free iodine. Used largely in medicine.

Potassium Bromide, KBr. *Prepared* like the iodide, except that bromine is used instead of iodine.

Properties. Colorless, cubical crystals or a granular powder, neutral in reaction. The commercial salt is usually white and slightly alkaline. Soluble in 1.5 parts water, 180 parts alcohol, 4 parts glycerine. Used largely in medicine.

Potassium Carbonate, K_2CO_3. (*Salt of tartar.*)

Preparation. Obtained in an impure form by lixiviation of wood ashes, evaporating the liquid to dryness and heating to redness as "*pearlash.*" Also made by the Leblanc process from the chloride. (See sodium carbonate.)

Properties. A white, granular, deliquescent power, soluble in water, of caustic taste and alkaline reaction. The salt can be obtained in a pure state by heating the bicarbonate thus:

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

Potassium Bicarbonate, $KHCO_3$. *Prepared* by passing carbon dioxide through a strong solution of potassium carbonate when crystals of the salt separate.

Properties. Colorless, flat, transparent crystals, slightly alkaline taste and reaction; soluble in 3 parts of water, insoluble in alcohol.

Potassium Nitrate, Nitre, Saltpeter, KNO_3. Found in nature in the soil in hot countries, being formed by the decay of nitrogenous organic matter in the presence of potassium salts.

Preparation. This salt is prepared by means of the *nitre bed,* which consists of heaps of nitrogenous organic matter—hides, horns, hoofs and flesh of dead animals—lime and earth. These are placed under a shed, watered with putrid urine and stirred from time to time to give access of the oxygen of the air. The chemical changes taking place here consist in the formation of ammonia, which is oxidized to nitric acid; the nitric acid uniting with lime forms calcium nitrate. The calcium nitrate is then washed out with water and decomposed with potassium carbonate, according to the equation:

$$Ca(NO_3)_2 + K_2CO_3 = CaCO_3 + 2KNO_3.$$

In this reaction, calcium carbonate precipitates, leaving potassium nitrate in solution. The solution is poured off and evaporated and potassium nitrate crystallizes out.

Potassium nitrate is made also by action of potassium chloride on sodium nitrate in solution, thus:

$$KCl + NaNO_3 = NaCl + KNO_3.$$

When solution of these salts is concentrated by evaporation to a specific gravity of 1.5 the sodium chloride crystallizes out first, being no more soluble in hot than cold water. The mother-liquor is then drawn off and potassium nitrate crystallizes upon cooling.

Properties. Colorless, transparent, six-sided rhombic prisms, or a crystalline powder; cooling saline taste, neutral reaction, soluble in 3.6 parts cold water, .4 parts boiling water, only slightly soluble in alcohol. The salt melts when heated to 353°, and at a higher temperature gives off oxygen. A strong oxidizing agent. Used in medicine; used as a preservative for meats; and used in making gunpowder.

Potassium Sulphate, K_2SO_4 Occurs in the salt mines of Stassfurt, and in plants.

Preparation. By action of sulphuric acid on the chloride, thus:

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl.$$

Properties. Anhydrous, rhombic prisms. Soluble in nine parts water; insoluble in alcohol; slightly bitter taste.

Potassium Bisulphate, Acid Sulphate of Potassium, $KHSO_4$, is obtained by the action of one molecule of sulphuric acid on one molecule of potassium chloride, thus:

$$H_2SO_4 + KCl = KHSO_4 + HCl.$$

Potassium Sulphite, $K_2SO_3.2H_2O$, is made by the action of sulphurous acid on potassium carbonate, thus:

$$H_2SO_3 + K_2CO_3 = K_2SO_3 + H_2O + CO_2.$$

Potassa Sulphurata, *Liver of Sulphur,* is a mixture of sulphides of potassium with sulphate and thiosulphate.

Prepared by heating a mixture of sulphur and potassium carbonate.

Properties. Liver-brown, irregular masses when fresh. Gradually turns yellowish-green, and finally gray by exposure, absorbing carbon dioxide.

Potassium Chlorate, $KClO_3$. *Prepared* by action of chlorine on *hot* solution of potassium hydroxide. Crystals are formed when the liquid cools.

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

Properties. Shining, transparent, tabular crystals or a white granular powder, soluble in sixteen parts of water, insoluble in absolute alcohol, cooling, saline taste. Gives up oxygen by heat. A strong, oxidizing agent.

Potassium Hypophosphite, KH_2PO_2. *Prepared* by action of calcium hypophosphite on potassium carbonate in solution, thus:

$$Ca(H_2PO_2)_2 + K_2CO_3 = 2KH_2PO_2 + CaCO_3.$$

The clear liquid is poured off and evaporated for crystals at a temperature not over 100°.

Properties. A granular, crystalline, deliquescent powder,

soluble in water and in alcohol. Explodes violently when rubbed with oxidizing agents.

Tests for Potassium.

1. To solution of potassium salt add a few drops of hydrochloric acid and of perchloride of platinum, a granular, yellow precipitate forms.

2. Solution of tartaric acid gives a colorless granular precipitate.

3. Sodium cobaltic nitrite in neutral solution gives a yellow precipitate.

4. Potassium colors the Bunsen burner flame violet, obscured by sodium, but can be seen through blue glass.

SODIUM (Natrium).

Symbol, Na. Atomic Weight, 23. Valence, I.

Discovered by Sir Humphrey Davy at about the same time and by the same means as potassium.

Occurrence in Nature. As the chloride, in rock salt, in large deposits in the earth, in mineral waters and in sea water. As the sulphate, carbonate and borate in minerals or in water. It is widely distributed in nature.

Preparation. According to the general rule for preparing the metals, by heating the carbonate with carbon in an iron retort:

$$Na_2CO_3 + C_2 = 3CO + Na_2.$$

The vapors of the metal are condensed in an iron receiver, and cooled under rectified petroleum.

Properties. Like potassium in appearance and consistency. It fuses at 95.6°; volatilizes at a red heat to a colorless vapor, which burns in the air with a yellow flame. Its specific gravity is .972. Sodium soon becomes tarnished by oxidation when exposed to the air, and has to be kept in petroleum. It acts upon

water like potassium, but less energetically, forming the hydroxide with liberation of hydrogen, which does not take fire unless the movements of the mass are restrained.

COMPOUNDS OF SODIUM.

Sodium Oxide, Na_2O. *Prepared* like the corresponding compound of potassium.

In *Properties* it is a gray, fusible, soluble mass.

Sodium Dioxide, Na_2O_2, is made by heating the metal in a stream of oxygen. It is a white powder, which decomposes when mixed with water into sodium hydroxide and water. When dissolved in water to which an acid has been added it forms peroxide of hydrogen and a sodium salt. This compound is used as a bleaching, disinfecting and oxidizing agent.

Sodium Hydroxide, *Caustic Soda,* NaOH. In method of *preparation* and *properties* like the hydroxide of potassium.

Sodium Chloride, *Common Salt,* NaCl. Found in large deposits in the earth, and obtained from this source by solution and crystallization. Found in sea water and removed by evaporation and crystallization, the remaining mother-liquor being known as "*bitturn,*" and used for preparation of bromine.

Sodium chloride is found in all parts of the animal system, where it facilitates the process of osmosis, and contributes to the formation of hydrochloric acid of the gastric juice.

Properties. Colorless, cubical crystals, which arrange themselves into pyramids. It has a salty taste, a neutral reaction, and is soluble in about 2.8 parts cold, or 2.5 hot water. It is anhydrous. The pure salt is not deliquescent, but the presence of magnesium chloride as an impurity causes it to absorb moisture from the air.

Sodium, bromide, iodide and *chlorate* are prepared like the corresponding compounds of potassium. The chlorate of sodium is more soluble in water than the potassium compound.

Sodium Sulphate, *Glauber's salt,* Na_2SO_4. Found in nature with the chloride, and in some mineral waters.

Preparation. By heating the chloride with sulphuric acid, and purifying by recrystallizing:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Properties. Sodium sulphate forms large, colorless crystals, containing 10 molecules water of crystallization; soluble in 2.8 parts cold water, and in .47 parts boiling water. Used as a purgative.

Sodium Bisulphate, $NaHSO_4$, made by the action of one molecule of sodium chloride upon a molecule of sulphuric acid, is a colorless, crystalline, soluble salt.

Sodium Sulphite, Na_2SO_3, and *Sodium bisulphite,* $NaHSO_3$. When a cold solution of sodium carbonate is saturated with sulphur dioxide the bisulphite separates in turbid crystals.

$$Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2.$$

By adding sodium carbonate to this bisulphite the normal sulphite is obtained as a crystalline, soluble salt, of alkaline reaction.

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + H_2O + CO_2.$$

Sodium Thiosulphate (*Sodium hyposulphite*), $Na_2S_2O_3$.

Prepared by boiling a solution of sodium sulphite with sulphur and crystallizing:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

Properties. Large, colorless, deliquescent, soluble crystals, containing five molecules water of crystallization. Used in photography to dissolve the halogen salts of silver.

Sodium Carbonate, *Washing Soda, Sal. Soda,* $Na_2CO_3 \cdot 10H_2O$. Found in nature in ash of plants, in mineral waters, in the soil in rainless countries.

Preparation. By the Leblanc process, which consists in heat-

ing sodium chloride with sulphuric acid in furnaces, and forming sodium sulphate, or "salt cake":

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The sodium sulphate is then heated in a furnace with limestone (calcium carbonate) and coal (carbon) to form "black-ash," which contains the sodium carbonate and calcium sulphide:

$$Na_2SO_4 + 4C + CaCO_3 = Na_2CO_3 + 4CO + CaS.$$

The "black-ash" is washed with water when calcium sulphide with calcium oxide forms an insoluble calcium oxysulphide, and sodium carbonate dissolves out, and is crystallized by evaporating the solution.

The *ammonia process,* or *Solvay method,* consists in the double decomposition effected by the action of ammonium bicarbonate on sodium chloride under pressure, and then heating the resulting sodium bicarbonate to convert it into carbonate thus:

$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Properties. Large, colorless, odorless crystals; specific gravity, 1.44; soluble in 1.6 parts of water, 1.02 parts of glycerine, and insoluble in alcohol. The salt has an alkaline taste and reaction, and loses water when exposed to the air. *Used* largely for cleansing purposes, in the manufacture of soap, and in medicine.

Sodium Bicarbonate, *Bread soda, Baking soda,* $NaHCO_3$. Found in nature in Vichy water.

Prepared by the ammonia soda process, or by passing carbonic acid gas over the carbonate containing some water, thus:

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3.$$

Properties. A white powder, soluble in water, insoluble in

alcohol. The aqueous solution is faintly alkaline, and is decomposed to carbonate by boiling.

Sodium Nitrate, $NaNO_3$. Occurs in nature in large deposits in South America, Chili, Peru, Brazil.

Prepared by purifying the crude salt by crystallization from water.

Properties. Colorless, odorless, transparent crystals; freely soluble in water, slightly soluble in alcohol. Deliquescent. *Used* largely for making nitric acid and potassium nitrate.

Sodium Orthophosphates. Three of these are known:

Monosodium phosphate, $NaH_2PO_4.H_2O$.

Disodium phosphate, $Na_2HPO_4.12H_2O$.

Trisodium phosphate, $Na_3PO_4.12H_2O$.

The last of these compounds is formed by adding caustic soda in excess to orthophosphoric acid. It is an unstable compound.

The second compound is the one commonly used in medicine as **Sodium Phosphate,** *Disodium hydrogen phosphate,* $Na_2HPO_4.12H_2O$.

Prepared by adding sodium carbonate to orthophosphoric acid to faintly alkaline reaction and crystallizing.

Properties. Large, colorless, odorless crystals, having a cooling, saline taste; soluble in water, insoluble in alcohol, and strongly efflorescent. Used as a purgative, and as a reagent.

The first compound, *monosodium phosphate,* is formed by adding phosphoric acid to the disodium phosphate to feebly acid reaction, and crystallizing.

Sodium Borate, *Borax,* $Na_2B_4O_7.10H_2O$. Found in nature in certain lakes—Thibet, Nevada, California—known as *tincal* in the crude state.

Prepared by crystallization from water.

Properties. Colorless, transparent crystals, or white powder; slightly alkaline taste and reaction. Slightly efflorescent, soluble

in water, insoluble in alcohol, soluble in glycerine. Loses water when heated, and finally forms borax bead. *Used* in medicine and in the arts.

Sodium Hypochlorite, NaClO. Employed in solution in "*liquor sodae chlorinatae,*" or Labaraque's solution.

Prepared by the action of calcium hypochlorite on sodium carbonate in solution. *Used* largely as an antiseptic and disinfectant.

Sodium Hypophosphite, $NaH_2PO_2.H_2O$. Preparation and properties like the corresponding salt of potassium.

Tests for Sodium.

1. All salts of sodium are soluble except the pyroantimoniate, therefore potassium pyroantimoniate is sometimes used as a reagent to precipitate its salts.

2. Sodium compounds color the flame yellow.

LITHIUM.

Symbol, Li. Atomic Weight, 7. Valence, I.

Occurs in nature as silicate and carbonate in minerals and some mineral waters. *Prepared* by electrolysis of fused chloride.

Properties. A white, soft, light metal, resembling potassium. Specific gravity .59.

The *bromide* and *carbonate* are the official inorganic salts. *Bromide* made by dissolving the carbonate in hydrobromic acid and crystallizing.

Properties. A white, granular, soluble powder.

The *carbonate* made by precipitating a solution of lithium salt with sodium carbonate.

Properties. A white powder, soluble in 80 parts of water, insoluble in alcohol.

The compounds of lithium are like those of potassium, but less soluble.

Tests. 1. Sodium phosphate, added to concentrated solution of lithium salts, gives a white precipitate on boiling.

2. Lithium salts color the flame crimson.

AMMONIUM.

Formula, NH_4. Molecular Weight, 18. Valence, I.

This compound radical is formed from ammonia, NH_3, by its action upon acids, in which the hydrogen of the acid is retained, thus:

$$NH_3 + HCl = NH_4Cl.$$

The chemical behavior of the ammonium radical is similar to that of an alkali metal, the radical acting like a single atom of a metal. The properties of its compounds show great resemblance to the compounds of potassium and sodium, and its metallic character is so well established that it is classed among the alkali metals.

Whenever an attempt is made to separate the ammonium radical, it decomposes into ammonia and hydrogen, so that this radical has never been obtained free. The formation of an ammonium amalgam is as near an approach to its separation as has yet been attained. Though ammonium amalgam has a decidedly metallic appearance, this interesting body soon decomposes into ammonia, hydrogen and mercury. The amalgam is made by dissolving metallic sodium in an equal amount of mercury, and adding the sodium amalgam to a strong solution of ammonium chloride. The chemical reaction is represented in the equation, thus:

$NaHg$	$+$	NH_4Cl	$=$	NH_4Hg	$+$	$NaCl.$
Sodium amalgam		Ammonium chloride		Ammonium amalgam		Sodium chloride

The ammonium compounds are obtained from the ammoniacal liquor of the gas-works, this liquid consisting of a solution of ammonium hydroxide in water. By saturating ammonium hy-

droxide with various acids the corresponding salts may be formed.

Ammonium Chloride, Sal-ammoniac, NH_4Cl. This salt is sometimes found in volcanic districts. *Preparation.* Ammonium chloride is formed by the action of hydrochloric acid upon the ammoniacal liquor of the gas-works, evaporating to dryness and further purifying by subliming. In *properties* it is found either in the form of a granular crystalline powder or in the form of tough crystalline masses. The salt is soluble in 3 parts cold water, one part hot water; it has a salty, disagreeable, metallic taste; when heated it sublimes without melting, and dissociates at a high temperature into NH_3 and HCl.

Ammonium Bromide, NH_4Br, and **Ammonium Iodide,** NH_4I, are prepared by adding solution of ammonium sulphate to potassium bromide for the first, and solution of ammonium sulphate to potassium iodide for the second, thus:

$$(NH_4)_2SO_4 + 2KBr = K_2SO_4 + 2NH_4Br.$$

Alcohol is then added to the mixture which precipitates potassium sulphate; the clear liquid is filtered off and evaporated, to obtain the ammonium salt.

Properties. Both of these salts are granular, crystalline solids; having a salty taste, and freely soluble in water or alcohol.

Decolorized tincture of iodine, made by adding ammonia water to tincture of iodine, contains ammonium iodide, ammonium iodate, and nitrogen iodide.

Ammonium Carbonate (*Sesquicarbonate*), $NH_4NH_2CO_2.NH_4HCO_3$. The formula for this compound shows that it is a double salt, made up of two compounds, ammonium carbamate, $NH_4NH_2CO_2$, and ammonium bicarbonate, NH_4HCO_3. Ammonium carbamate is a salt of carbamic acid, $H\,NH_2CO_2$, in which the hydrogen has been replaced by the radical NH_4.

This acid will be considered in the study of organic chemistry.

Preparation. Ammonium carbonate is obtained by subliming a mixture of ammonium chloride and calcium carbonate, according to the following equation:

$$4NH_4Cl + 2CaCO_3 = NH_4NH_2CO_2.NH_4HCO_3 + NH_3 + H_2O + 2CaCl_2.$$

Properties. Ammonium carbonate occurs in colorless, crystalline masses; having an alkaline taste and reaction, the odor of ammonia, and being soluble in water. By exposure to air the salt gradually undergoes decomposition, the crystals becoming covered with a white coating until they gradually fall to a white, granular powder. This decomposition consists in elimination of the ammonium carbamate from the molecule, which escapes as $2NH_3$ and CO_2, leaving ammonium bicarbonate behind as the white granular powder.

The tendency of ammonium carbonate to undergo decomposition requires the exercise of care in selecting the salt for use in medicine; the undecomposed crystals alone should be used for this purpose, and they may be easily recognized by their colorless, crystalline, semitransparent appearance.

The normal carbonate of ammonium, $(NH_4)_2CO_3$, can be formed from the sesquicarbonate by dissolving this salt in water and adding ammonia water to the solution. When ammonium sesquicarbonate is dissolved in water the carbamate portion of the molecule is converted into normal salt, and when ammonia water is added to this solution the remaining portion of the molecule is converted into normal ammonium carbonate. These chemical changes are represented in the following equations:

$$NH_4NH_2CO_2.NH_4HCO_3 + H_2O = (NH_4)_2CO_3 + NH_4HCO_3.$$

$$(NH_4)_2CO_3 + NH_4HCO_3 + NH_4OH = 2(NH_4)_2CO_3 + H_2O.$$

Ammonium carbonate is used in medicine and as a chemical reagent.

Aromatic Spirit of Ammonia is a solution of normal ammonium carbonate in diluted alcohol flavored with essential oils.

Ammonium Sulphate, $(NH_4)_2SO_4$; **Ammonium Nitrate,** NH_4NO_3; **Ammonium Nitrite,** NH_4NO_2; **Ammonium Phosphate,** $(NH_4)_2HPO_4$. These salts are prepared by the action of the corresponding acid upon ammonia water, evaporating carefully and crystallizing. They are all white, solid, soluble salts.

Ammonium nitrate decomposes, when heated, into nitrogen monoxide, N_2O, and water, and is used in making "laughing gas."

Ammonium nitrite when heated decomposes into nitrogen and water.

Ammonium Sodium Hydrogen Phosphate, *Microcosmic Salt, Salt of Phosphorus,* NH_4NaHPO_4 is found in guano and decaying urine.

Prepared by mixing solutions of sodium phosphate and ammonium chloride and crystallizing:

$$Na_2HPO_4 + NH_4Cl = NH_4NaHPO_4 + NaCl.$$

Properties. Granular, prismatic crystals, very soluble. Used in chemical analysis.

Ammonium Hydrogen Sulphide, *Ammonium Sulphydrate or Hydrosulphide,* NH_4HS. A salt formed by replacement of one of the hydrogen atoms of hydrogen sulphide, H_2S, with the ammonium radical.

Prepared by passing hydrogen sulphide into dilute ammonia water:

$$NH_4OH + H_2S = NH_4HS + H_2O.$$

Properties. Usually seen in the form of solution which is colorless or has a slightly greenish tinge; it has the odor of ammonia and of hydrogen sulphide. When ammonia water is added to this solution it is converted into normal ammonium sulphide, thus:

$$NH_4HS + NH_4OH = (NH_4)_2S + H_2O.$$

These salts may be obtained in the form of a white crystalline mass, which soon decomposes. Ammonium sulphide is very largely used as a reagent for precipitation of the heavy metals.

Tests for Ammonium Compounds.

1. All the compounds of ammonium are volatile, either with or without decomposition.

2. When heated with alkalies, ammonia gas is given off. The ammonia gas may be recognized by its odor; by its action on moistened litmus paper, which it turns blue; by the white fumes produced in the presence of hydrochloric acid.

3. Solution of perchloride of platinum and hydrochloric acid give a fine granular yellow precipitate.

4. Nessler's reagent[1] gives a reddish-brown color or precipitate.

5. Sodium cobaltic nitrite in neutral or acid solution gives a yellow precipitate.

Analytical Reactions.

A. Directions for the detection of *one* of the metals, potassium, sodium or ammonium in aqueous solution.

1. Take a small portion of the solution (about 2 c.c.) in a test-tube, add a few drops of solution of caustic soda and heat gently in the flame of the Bunsen burner. The odor of ammonia will indicate the presence of ammonium compounds.

2. If ammonium be absent, take another portion of the solution in a test-tube and add a few drops of hydrochloric acid and

[1] Nessler's Reagent is made by adding to a solution of 5 grammes of potassium iodide in hot water, a hot solution of mercuric chloride—2.5 grammes in 10 c.c. water. To the turbid red mixture is added a solution containing 16 grammes of potassium hydroxide in 40 c.c. of water, and the whole is diluted to 100 c.c. This mixture is allowed to stand and the clear supernatant liquid is decanted for use. The reagent improves by keeping.

perchloride of platinum. A granular yellow precipitate indicates the presence of potassium.

The perchloride of platinum test for potassium cannot be applied in the presence of ammonium salts.

3. The loop of a platinum wire dipped in a little hydrochloric acid and then into some of the solution will give the intense yellow light of sodium, when held in the flame, if that element be present.

B. Directions for detection of *one, two* or all *three* of the metals potassium, sodium or ammonium in aqueous solution of their salts.

1. Test a small portion of the original solution for ammonium compounds, as directed in " I " of the foregoing experiments. If ammonium salts be present make a note of the fact and proceed to remove the salts of this element by evaporating the original solution to dryness in a porcelain dish, and then carefully heating the dry residue in a fume chamber until white fumes of ammonium salts cease to be evolved.

2. After the contents of the dish have cooled, the residue is dissolved in a small quantity of water and tested for potassium by the perchloride of platinum test. In the absence of ammonium the original solution may be tested at once for potassium.

3. Apply the flame test to some of the original solution for sodium.

MAGNESIUM GROUP.

MAGNESIUM.

Symbol, Mg. Atomic Weight, 24. Valence, II.

Magnesium and the rare metal Beryllium form a group of elements known as the magnesium group. They decompose hot water slowly, with evolution of hydrogen. They form insoluble oxides, hydroxides, carbonates, phosphates and arsenates.

These metals resemble zinc in the solubility of the sulphate and the volatility of the chloride, but differ from that metal in the fact that the sulphide is not precipitated by ammonium sulphide.

Magnesium is found abundantly in nature and widely distributed. In the mineral kingdom it is found as sulphate, chloride, carbonate, silicate and phosphate. As carbonate it is found in *magnesite;* as double carbonate of magnesium and calcium, in *dolomite;* as silicate, it is found in *meerschaum, talc, asbestos, soapstone,* etc. It is found in certain mineral waters known as bitter waters, as chloride and sulphate. In the animal and vegetable kingdoms magnesium occurs as carbonate in bones, and as phosphate in cereals; also with vegetable acids in plants.

Preparation. By electrolysis of the fused chloride, or by heating the chloride with sodium.

Properties. A bright, silvery-white metal; sp. gr. 1.75; tenacious, ductile; when heated may be rolled into ribbon or drawn into wire. It melts at 800°, and volatilizes at a red heat; oxidizes in moist air and becomes covered with a coating of oxide and carbonate; burns when heated in air with intense white light forming the oxide which is non-fusible. It decomposes hot water; is dissolved by dilute acids, but not affected by alkalies. It is bivalent in its compounds. Used in photographing dark chambers.

Magnesium Oxide, *Calcined Magnesia,* MgO. (*Magnesia.*)

Preparation. By burning magnesia, or by heating the carbonate or hydroxide.

$$MgCO_3 = MgO + CO_2.$$

Properties. A white, amorphous, insoluble powder; unites with water to form the hydroxide.

Magnesia occurs in two forms, light and heavy oxide, made by heating the light and heavy carbonate, respectively.

Magnesium Hydroxide, $Mg(OH)_2$.

Preparation. By adding KOH, or NaOH to solution of a magnesium salt, collecting, washing and drying the precipitate.

Properties. A white, amorphous powder, nearly insoluble in water; soluble in solution of ammonium chloride. Absorbs CO_2 from air to form carbonate.

Milk of Magnesia is a white, opaque liquid, consisting of magnesium hydroxide suspended in water.

Magnesium Chloride, $MgCl_2$. Found in mineral springs in small quantity.

Prepared by dissolving the carbonate or hydroxide in HCl, and evaporating. Crystallizes with 6 molecules of water, freely soluble, and deliquescent. When heated to drive off the water of crystallization it decomposes. To obtain the anhydrous salt evaporate mixed solutions of $MgCl_2$ and NH_4Cl to dryness, and heat to 460°, when the water and ammonium chloride are driven off, leaving the anhydrous salt in leafy crystals.

Magnesium Carbonate, $MgCO_3$ (*Magnesia Alba, Light Magnesia*). Occurs in nature as magnesite in crystalline compact masses, and with calcium in dolomite. The official carbonate is a mixture of carbonate and hydroxide.

Prepared by boiling solution magnesium sulphate and solution sodium carbonate, collecting, washing and drying the precipitate:

$$5MgSO_4 + 5Na_2CO_3 + 6H_2O = 5Na_2SO_4 + 4MgCO_3.Mg(OH)_2.5H_2O + CO_2.$$

If the above mixture of precipitate and solution be evaporated to dryness and the sodium sulphate be washed out with water, the remaining magnesium carbonate constitutes the *dense, or heavy magnesium carbonate.*

In properties magnesium carbonate is a white, amorphous, insoluble powder. By suspending the normal salt in water and passing carbon dioxide through the mixture, crystals of normal carbonate form and separate.

Magnesium Sulphate, *Epsom Salt,* $MgSO_4$. Found in sea water, in mineral springs, and in the mineral *kieserite.*

Prepared by action of sulphuric acid on the carbonate and evaporating the resulting solution to obtain crystals.

$$MgCO_3 + H_2SO_4 = MgSO_4 + CO_2 + H_2O.$$

Properties. Colorless prismatic crystals, containing 7 molecules water of crystallization. Saline, bitter taste, freely soluble in water (2 parts at 0°), neutral reaction. At 150° loses all the water of crystallization but one molecule, which comes off at 200°—this last molecule known as the water of constitution. Use as a purgative in medicine. (Crystals isomorphous with the sulphate of zinc.)

Magnesium Phosphate, $MgHPO_4$, forms in colorless crystals when sodium phosphate is added to a solution of magnesium sulphate. When ammonia water is added to the solution of magnesium sulphate and sodium phosphate solution is poured in, a double compound of $MgNH_4PO_4$ precipitates. This magnesium ammonium phosphate is slightly soluble in water, but insoluble in ammonia water. This reaction used as a test for magnesium.

Tests for Magnesium.

(1) NaOH, KOH, or NH_4OH, give precipitate of $Mg(OH)_2$, white and gelatinous, insoluble in excess, but soluble in solution of NH_4Cl, or ammonium salts.

(2) K_2CO_3, or Na_2CO_3 gives, when heated with Mg compounds, white precipitate of carbonate. $(NH_4)_2CO_3$ gives no precipitate.

(3) Add sol. NH_4Cl, NH_4OH and Na_2HPO_4; a white precipitate of $MgNH_4PO_4$ forms:

$$Na_2HPO_4 + MgSO_4 + NH_4OH = MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

BERYLLIUM.

Symbol, Be. Atomic Weight, 9. Valence, II.

Occupies a position in this group similar to that held in the group of alkalies by lithium.

Occurs in nature as silicate.

Prepared by heating the chloride with Na.

Properties. A silvery-white metal, malleable and ductile, little affected by air.

Its salts resemble those of Mg. They have a sweet taste, and for this reason the element is sometimes called glucinum.

Only of scientific interest.

ALKALINE EARTH METALS.

Calcium, $Ca'' = 40$. **Strontium,** $Sr'' = 87$. **Barium,** $Ba'' = 136$. The metals of this group are called alkaline earth metals because they resemble in their properties the alkalies, on the one hand, and the earths on the other. This is shown very strongly in the oxides which like those of alkalies form hydroxides with water, and like those of the earths can be made from the hydroxide. With increase of atomic weight from calcium to barium their chemical energy and basic properties become greater. They decompose water with liberation of hydrogen, as do the alkalies, but differ from them in forming insoluble carbonates and phosphates and almost insoluble sulphates. They differ from the earth metals by the solubility of their hydroxides. They are all bivalent.

CALCIUM.

Symbol, Ca. Atomic Weight, 40. Valence, II.

Occurrence in Nature. Calcium is widely distributed over the surface of the earth. It occurs as calcium carbonate in limestone, marble and chalk; as sulphate in gypsum and alabaster; as phosphate it constitutes apatite; as fluoride it is found in fluorspar; as silicate in rocks. Calcium is found in the bones and nervous tissues of animals as phosphates; also in plants in the same form of combination, and in union with organic acids.

Preparation. On account of the infusibility of the oxide, calcium is more difficult to separate than the alkalies. It is usually prepared by electrolysis of the fused chloride, since the oxide when heated with carbon will not avail on account of its great infusibility.

Properties. A yellow shining metal, resembling gold, quickly tarnishing by exposure to moist air. It decomposes water, is easily fused, and when heated in air it burns with a yellow flame.

COMPOUNDS OF CALCIUM.

The halogen salts are prepared by dissolving the oxide or carbonate in the haloid acids, or by direct union of calcium with the elements. The metal burns in an atmosphere of chlorine, bromine or iodine vapors.

Calcium Chloride, $CaCl_2$. This salt crystallizes from aqueous solution with six molecules of water in large deliquescent prismatic crystals. When heated it melts in its water of crystallization, and at 200° becomes anhydrous as a white porous mass. The dry salt has strong affinity for water and is largely used for drying gases. Calcium chloride is often used for production of low temperature by dissolving hydrous salt in water; calcium chloride and snow, or powdered ice, gives a temperature of —48° C.

The *bromide* and *iodide* are similar in physical and chemical properties to the chloride.

Calcium Oxide, CaO, *Burned lime, Quick-lime.* May be made by heating the nitrate or carbonate. Generally *prepared* by burning the carbonate as found in limestone ($CaCO_3$) in lime-kilns, at a temperature of 800° C.

$$CaCO_3 = CaO + CO_2.$$

The limestone retains its original size and shape but loses weight.

Properties. Calcium oxide occurs as a white, odorless, amorphous, infusible mass; having an alkaline taste and reaction. It has a powerful affinity for water with which it unites and falls to a grayish-white powder of calcium hydroxide, and it is then designated by the term *slaked lime.* Air slaked lime is formed by exposure of calcium oxide to the air, when it absorbs water and carbon dioxide, forming the hydroxide and carbonate. The calcium light is obtained by causing the flame of the oxyhydrogen blowpipe to fall upon lime, thus heating the salt to the degree of incandescence.

Calcium dioxide can be precipitated by adding H_2O_2 to lime water.

Calcium Hydroxide, Slaked Lime, $Ca(OH)_2$, is a grayish-white, amorphous powder; it forms a paste with water, known as milk of lime; it is slightly soluble in water, about one part in 760 of water, more soluble in cold than hot water.

Lime Water is prepared by shaking one part of calcium hydroxide with 30 parts of water, allowing the lime to settle and pouring off the clear liquid; to the residue, 300 parts of pure water are added, the mixture thoroughly shaken and allowed to settle, the clear liquid is then decanted for use. Lime water is a clear, colorless liquid; having a feebly alkaline taste and reaction; it absorbs carbon dioxide gas from the air

and forms a thin transparent pellicle, or crust, of calcium carbonate upon its exposed surface. A stream of carbon dioxide passed through the liquid causes precipitation of the calcium as carbonate.

Calcium Carbonate, $CaCO_3$, occurs in nature in great abundance; it is found as dolomite; as limestone, which, when granular and crystalline, is called marble; as calcite, which, when pure and crystalline, is known as Iceland spar and is used for making lenses for optical instruments. It is found, also, as oyster shells, coral, egg shells and chalk.

The precipitated carbonate of calcium, used in medicine, is formed by adding sodium carbonate to calcium chloride in solution; it is a white, amorphous, insoluble powder. The carbonate of calcium is insoluble in pure water, but soluble to some extent in water containing carbon dioxide, for this reason it often occurs dissolved in natural waters, and when these are boiled the carbon dioxide is expelled and the carbonate is precipitated. The formation of stalactites, and of incrustations on the interior of boilers is due to the precipitation of calcium carbonate following the expulsion of carbon dioxide.

Calcium Sulphate, $CaSO_4$, occurs in nature as *gypsum,* with two molecules of water of crystallization. It is prepared by adding sulphuric acid to a concentrated solution of calcium chloride, when it precipitates from solution; the precipitate is removed by filtration and dried.

Properties. A white, nearly insoluble powder, one part requiring 400 to 500 parts of water for solution. By heating the naturally occurring salt to about 110°, water is driven off and anhydrous calcium sulphate remains; this compound, when ground to an impalpable powder, is known as "plaster of Paris." The "setting" of plaster of Paris is due to its chemical union with water.

Calcium Nitrate, $Ca(NO_3)_2$, is produced in nature by decay of nitrogenous organic matter in presence of lime.

Preparation. By the action of diluted nitric acid on calcium carbonate, evaporating and crystallizing the solution.

Properties. Colorless crystals, soluble in water. Used in making potassium nitrate.

Calcium Phosphate, Tricalcium Phosphate, $Ca_3(PO_4)_2$. Occurs in nature in deposits in the earth as apatite; also found in bones and teeth of animals. Can be made from bone ash by action of hydrochloric acid, which dissolves the salt; it is then precipitated by adding ammonia water.

Preparation. Prepared by adding Na_2HPO_4 and ammonia water to solution $CaCl_2$:

$$2Na_2HPO_4 + 3CaCl_2 + 2NH_4OH = Ca_3(PO_4)_2 + 4NaCl + 2NH_4Cl + 2H_2O.$$

Properties. Tasteless, amorphous, insoluble powder.

Superphosphate, or Acid Phosphate of Calcium, $CaH_4(PO_4)_2$. Made by digesting the tricalcium phosphate with sulphuric acid, and occurs as a soluble deliquescent salt. Its formation is shown by the equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$

This salt is present in certain "baking powders," and in an impure form with calcium sulphate in fertilizer.

Bone Ash is formed by burning bones, and consists of the inorganic, non-volatile constituents of bones, chiefly tricalcium phosphate.

Bone Black is *bone charcoal,* formed by destructive distillation of bones, and contains carbon in addition to what is found in bone ash.

Chlorinated Lime, Calcium Hypochlorite, *Bleaching Powder* (*Chloride of Lime*). Probably, $Ca(ClO)_2.CaCl_2.2H_2O$, a molecular compound of chloride and hypochlorite of calcium.

Prepared by passing chlorine over dry calcium hydroxide at the ordinary temperature of the air:

$$2Ca(OH)_2 + 2Cl_2 = Ca(ClO)_2.CaCl_2 + 2H_2O.$$

Properties. A white, soluble, deliquescent powder, exhaling the odor of hypochlorous acid, and decomposed by exposure to air. It gives off chlorine when acted upon by acids, and should contain not less than 30 per cent. of available chlorine.

Used largely as a bleaching and disinfecting agent, and for obtaining chlorine.

Calcium Carbide, CaC_2, is prepared by melting a mixture of powdered calcium oxide and coke-dust in an electric furnace.

Properties. It occurs in dark-colored masses, having a metallic appearance, and giving off the odor of acetylene by absorption of atmospheric moisture. It is used in preparation of acetylene for illuminating purposes, by the action of water, thus:

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

Tests for Calcium.

1. Solutions of calcium salts give a white precipitate with the carbonates of potassium, sodium (or ammonium).

2. Sodium phosphate gives a white precipitate in neutral solutions.

3. Ammonium oxalate gives a white precipitate, insoluble in acetic, soluble in hydrochloric acid.

4. Sulphates in strong solution give a white precipitate.

5. A reddish-yellow color is imparted to the flame. Ammonia water gives no precipitate.

STRONTIUM.

Symbol, Sr. Atomic Weight, 87. Valence, II.

History. Named for the village of Strontium, in Scotland, where a compound of the metal was first detected. The metal was separated by Sir Humphrey Davy in 1808.

Occurrence in Nature as the carbonate in *strontianite,* and as sulphate in *celestite.* Found frequently with calcium.

Preparation. By electrolysis of the fused chloride.

Properties. A yellow, ductile metal; specific gravity, 2.5.

It decomposes water, oxidizes in the air, and burns with a bright light when heated, imparting a red color to the flame.

Strontium compounds are like those of calcium, except that they are more basic in character and properties.

Strontium Oxide is obtained by heating the nitrate, and is like calcium oxide in properties. The *Hydroxide* is more soluble in water than the corresponding salt of calcium.

The *Strontium Bromide,* $SrBr_2$, and *Strontium Iodide,* SrI_2, are both official. These salts, as well as the nitrate and chloride, may be obtained by dissolving the carbonate in the respective acids and crystallizing. They are white, soluble compounds.

Strontium nitrate is largely used in pyrotechnics to form "red fires."

Tests for Strontium.

1. Solutions of strontium compounds with solutions of carbonates, oxalates, and phosphates, give a white precipitate.
2. Sulphates give a white precipitate.
3. Potassium chromate gives a pale-yellow precipitate, soluble in acetic and hydrochloric acid.
4. Potassium dichromate gives no precipitate; differing from barium.

BARIUM.

Symbol, Ba. Atomic Weight, 136. Valence, II.

Occurrence in Nature in large masses, as *heavy spar,* or barium sulphate, and as *witherite,* or barium carbonate. Compounds of barium are distinguished by their high specific gravity. The basic properties of barium are more strongly developed than they are in calcium or strontium. The salts of barium can be prepared from the carbonate by the action of the appropriate acid. The sulphate of barium is sometimes employed for preparation of other salts. This is done by first heating with carbon to form the sulphide, and then dissolving the sulphide in the appropriate acid.

Preparation. By electrolysis of the fused chloride.

Properties. A bright, yellow metal; specific gravity 3.6; rapidly oxidizes in the air; decomposes water like sodium.

Barium Chloride, $BaCl_2$, is of interest because it is largely used as a reagent to precipitate the soluble sulphates from solution. It is prepared by dissolving barium carbonate in diluted hydrochloric acid, evaporating and crystallizing.

Properties. Clear, colorless crystals, containing two molecules of water of crystallization; permanent in the air; soluble in water; poisonous, like all soluble salts of barium.

Barium Oxide, BaO, is prepared by heating the nitrate. It is a grayish-white, amorphous mass; specific gravity 5.5; fusible in the oxyhydrogen flame; unites with water with evolution of heat to form the hydroxide.

Barium Dioxide, BaO_2, is prepared by heating the oxide to dull redness in air or oxygen. When heated to a still higher temperature it gives up oxygen and again becomes the monoxide; on account of this property, it has been employed in the manufacture of oxygen, but the power of the oxide to absorb and give up oxygen disappears after a time.

Properties. Barium dioxide is a grayish-white solid, slightly soluble in water, forming the hydroxide; it is used for making hydrogen dioxide by adding water and a mineral acid, as shown in the equations:

$$BaO_2 + 2HCl = H_2O_2 + BaCl_2.$$

$$BaO_2 + H_2O + CO_2 = H_2O_2 + BaCO_3.$$

Barium Hydroxide, $Ba(OH)_2$, is prepared by slaking the oxide, or by precipitating a strong solution of barium salt by sodium or potassium hydroxide.

Properties. An amorphous, white powder; soluble in 20 parts of water; the solution in water gives a strongly alkaline liquid, known as *baryta water.* At a red heat the hydroxide

fuses and solidifies to a crystalline mass on cooling, like caustic potash.

The other salts of barium are made by dissolving the carbonate in the respective acids, and are like the corresponding calcium salts in properties. The sulphate is insoluble in water and acids.

Toxicology. The soluble salts of barium act as poisons, producing vomiting, diarrhoea, albuminuria, haematuria and convulsions preceding death. The antidote is a weak solution of sulphuric acid, or other suitable sulphate, in order to form the insoluble barium sulphate.

Tests for Barium.

1. Carbonates, phosphates or oxalates of alkalies give white precipitate.

2. Sulphuric acid or sulphates give white precipitate insoluble in dilute acids.

3. Potassium chromate and dichromate give a pale yellow precipitate soluble in HCl.

4. Compounds color the flame pale yellowish-green.

Radium. This element, which has not as yet been obtained in the free state, is best known in the form of its bromide or chloride, and the name radium is commonly applied to these salts. The element belongs to the group of the alkaline earth metals, and it stands next to thorium in Mendelejeff's system of classification. As determined by Madam Curie, it has the atomic weight of 225.

Radium is obtained from the mineral pitchblende, and it is associated in this mineral with uranium, polonium, actinium and thorium. Radium chloride is prepared from the residue of pitchblende, after the separation of uranium salts, by repeated crystallization upon treating with hydrochloric acid. The rarity and consequent high price of the salt is due to the immense amount of labor involved in its preparation.

The salts of the elements uranium, thorium, polonium, actinium and radium emit a form of energy which has the power to affect the photographic plate, and is luminous in the dark. Investigations point to the conclusion that there are both visible and invisible emanations from these, so-called, radio-active bodies; the fluorescent, or visible rays, being accompanied by invisible forms of energy, the latter having been referred to as "dark light." The property of fluorescence first called

attention to these qualities, and the power of pitchblende to affect the photographic plate in the dark led to the investigations which resulted in the discovery of radium.

The opinion of scientists inclines to the belief that the emanations from radium are, at least in part, of a material character, and that they are of three kinds: (1) Real atoms, much larger than the free electrons, and positively electrified. These are easily checked in passing through obstructions, they cause air to become a conductor and they act on the photographic plate. (2) Free electrons, or matter identical with the cathode stream in the ultra-gaseous state. (3) Rays having high power of penetration, and believed by some to be like the Roentgen rays.

In giving expression to the degree of radio-activity of radium, the standard, or unit of comparison, is the amount of activity in metallic uranium, taken as one. It is claimed that an activity of over one and three quarter millions has been obtained for radium.

Radium is luminous in the dark, its temperature is above that of the surrounding air, and it is capable of melting its own weight of ice every hour. When kept near the skin in a glass tube for some time it causes painful ulceration which is slow to heal. Animal and bacterial life continuously exposed to its rays are weakened or destroyed.

Analytical Reactions.

Directions for analysis of an aqueous solution containing one or all of the metallic elements hitherto considered.

To the solution add NH_4Cl, NH_4OH, $(NH_4)_2CO_3$, boil and filter.

<table>
<tr><td colspan="2">Precipitate.
Ba, Ca, Sr.
Wash, dissolve in acetic acid, add $K_2Cr_2O_7$, and filter.</td><td colspan="2">Filtrate.
Mg, NH_4, Na, K, Li.
Add $(NH_4)_2HPO_4$ and filter.</td></tr>
<tr><td>Ppt.
Ba,
Yellow.</td><td colspan="2">Filtrate.
Ca, Sr.
Neutralize with ammonia water and add K_2CrO_4</td><td>Precipitate.
Mg, as $MgNH_4HPO_4$.</td><td>Filtrate.
NH_4, Na, K.
Evaporate to dryness, ignite, test dry residue for sodium and lithium by flame test on platinum wire.
Dissolve residue in water and test for potassium by $PtCl_4$.
Test original solution for ammonium.</td></tr>
<tr><td></td><td>Ppt.
Sr,
Pale yellow.</td><td>Filtrate.
Ca.
Add ammon. oxalate: Ca ppts. white as oxalate.</td><td></td><td></td></tr>
</table>

In the above analysis the addition of ammonium chloride serves to retain the magnesium salts in solution, the ammonium hydroxide to neutralize any acid which might be present, the ammonium carbonate serving as the essential precipitating agent.

THE EARTH METALS.

Aluminum, Cerium and a Number of Rare Metals.

ALUMINUM.

Symbol, Al. Atomic Weight, 27. Valence, III.

Occurrence in Nature. One of the most widely distributed elements in nature. Generally found in the solid mineral portion of the earth; hardly ever in the vegetable or animal kingdoms. Found as the *oxide* crystallized in ruby, sapphire and corundum more or less colored by other substances; also as *silicate* in clay, mica, slate, granite and in silicated rocks.

Preparation. By heating the chloride with sodium. Aluminum is extensively prepared by electrolysis of the double fluoride of aluminum and sodium, to which aluminum oxide is added as the operation proceeds.

Properties. A silver-white metal, very ductile and malleable; specific gravity, 2.67, a light metal; fuses at a red heat, but will not volatilize; not affected by dry air, burns when thin sheets are heated in oxygen. Nitric or sulphuric acid will not affect aluminum in the cold; it is dissolved, however, by hydrochloric acid. It dissolves in potassium or sodium hydroxide solution.

Aluminum is capable of taking a high polish, and this, with its property of permanence in the air, fit it for use in making ornamental articles and vessels. It is also used in making scientific instruments. Aluminum bronze contains ten per cent. of aluminum and ninety per cent. of copper. Aluminum is a trivalent element, but two atoms usually go together exerting the quantivalence of six.

Aluminum Chloride, Al_2Cl_6, may be prepared in solution by dissolving aluminum in hydrochloric acid, from which it crystallizes with six molecules of water. If this salt be heated with

the view of obtaining the anhydrous chloride it is decomposed into hydrochloric acid and aluminum oxide. To prepare the anhydrous chloride, heat a mixture of aluminum oxide and carbon and pass chlorine over this. The simultaneous action of carbon and chlorine on the Al_2O_3 results in the formation of the chloride.

$$Al_2O_3 + 3C + 3Cl_2 = 3CO + Al_2Cl_6.$$

The chloride can also be formed by the action of chlorine on the heated metal. *In properties* aluminum chloride is a deliquescent, soluble, crystalline solid. The anhydrous salt is used in making metallic aluminum.

Aluminum Oxide, Al_2O_3. Found in nature crystallized with coloring matter, as ruby, sapphire, and impure as emery.

Prepared by heating the hydroxide:

$$Al_2(OH)_6 = Al_2O_3 + 3H_2O.$$

Properties. A white, amorphous, insoluble powder; fuses to a transparent mass in the oxyhydrogen flame. To render it soluble for analysis is fused with caustic alkalies.

Aluminum Hydroxide, $Al_2(OH)_6$. *Prepared* by adding ammonia water to solution of aluminum salt, or by adding a solution of alkaline carbonate to the same:

$$Al_2(SO_4)_3 + 6NH_4OH = Al_2(OH)_6 + 3(NH_4)_2SO_4, \text{ or } Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = Al_2(OH)_6 + 3Na_2SO_4 + 3CO_2.$$

Explanation of formation of hydroxide instead of carbonate by above reaction is found in the fact that aluminum is too feeble a base to combine with this weak acid.

Properties. A white gelatinous precipitate. When fresh, soluble in acids and alkalies; when washed and dried, nearly insoluble in acids, and a white powder.

Aluminum hydrate is used in the process of dyeing to fix the coloring matter to the fabric of cloth; it has an affinity for

organic and inorganic coloring matter, and also an affinity for the organic material of which cloth is manufactured; on account of these properties it fixes the dye, and such action is known as that of *a mordant*—(*Mordeo, to bite*).

Aluminum hydroxide shows a feebly acidic tendency when brought in the presence of powerful alkalies like sodium and potassium; with potassium it forms an aluminate, in which the metal takes the part of an acid radical, as shown by the formula, $KAlO_3$, potassium aluminate.

Aluminum Sulphate, $Al_2(SO_4)_3$. *Prepared* by dissolving the hydroxide in sulphuric acid, or by digesting sulphuric acid with clay and evaporating the solution.

Properties. A white, crystalline powder; soluble in water. It has power to combine with sulphates of alkalies to form double salts, thus:

$$K_2SO_4.Al_2(SO_4)_3.24H_2O.$$

Alums. A general term applied to salts consisting of a molecule of the sulphate of a univalent element, with a molecule of the sulphate of a trivalent element, and twenty-four molecules water of crystallization:

$K_2SO_4.Al_2(SO_4)_3.24H_2O$,	Potassium Aluminum Alum.
$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$,	Ammonium Aluminum Alum.
$K_2SO_4.Cr_2(SO_4)_3.24H_2O$,	Potassium Chromium Alum.
$(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$,	Ammonium Iron Alum.

Official Alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$.

This salt is prepared by making a solution of aluminum sulphate, as described above, mixing this with a solution of potassium sulphate and evaporating the liquid for the formation of cystals.

Properties. Large, eight-sided, colorless crystals; sweetish, astringent taste; acid reaction. Soluble in nine parts water, 0.3 parts boiling water. The crystals, when exposed to the air, will absorb ammonia and their surfaces become white.

Dried Alum, *Alumen Exsiccatum, Burnt Alum.* Alum from which water of crystallization has been expelled by heat. A white powder, soluble in hot water; slowly soluble in cold water.

Aluminum Silicates. These are found in nature with potassium and sodium, as felspar; and as mica and granite, with calcium. A gradual disintegration of these minerals results in removal of the sodium and potassium to the soil, the insoluble silicates being left behind, with water, constituting clay. These compounds are usually colored by iron salts. Pure clay, free from iron salts, is called kaolin, or porcelain clay. Earthenware is made by moulding clay, and heating to expel water.

Porcelain is made of kaolin mixed with felspar, or potassium aluminum silicates, which when heated, furnish the glaze. *Glass* is the silicate of calcium and sodium, crown glass; or of calcium and potassium, Bohemian glass; or of potassium and lead, flint glass. *Crown glass,* the silicate of calcium and sodium, is the ordinary window-glass, it has a greenish tinge due to the presence of small amounts of iron salts. *Bohemian, or potash calcium glass,* is very infusible, and resistant to the action of acids and alkalies, and for these reasons it is largely used in the laboratory. *Flint glass,* potassium lead silicate, is remarkable for its density, lustre, and refractive power. It is the most fusible and readily attacked by chemicals.

Ultramarine (Lapis Lazuli). This was formerly obtained solely as a valuable mineral, but is now made by artificial means. Its exact composition is not known, but it contains aluminum and sodium silicate, and sodium polysulphides. Made by heating together sodium carbonate, sodium sulphate, clay, carbon and sulphur.

Tests for Aluminum.

1. Sodium, or potassium hydroxide gives a gelatinous precipitate of aluminum hydroxide, soluble in excess. Ammonia water gives the same precipitate, insoluble in excess.

2. Sodium, or potassium, carbonate gives a precipitate of aluminum hydroxide, with escape of carbon dioxide.

3. Ammonium sulphide gives same precipitate as in 2, with escape of H_2S:

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = Al_2(OH)_6 + 3(NH_4)_2SO_4 + 3H_2S.$$

4. Sodium phosphate gives white precipitate, soluble in acids except acetic.

Cerium, Ce = 139. *Occurrence* as silicate in cerite; not abundant. Salts resemble those of aluminum. *Ammonium* oxalate forms a precipitate of *cerium oxalate* with solutions of cerium.

The *oxalate* is a white, insoluble, granular powder, given internally for nausea. Salts of cerium heated to redness and residue of oxide dissolved in sulphuric acid, gives a blue color with a crystal of strychnine, which turns purple and then red.

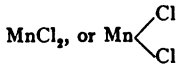
Cerium salts precipitate the hydroxide on adding $(NH_4)_2S$, NH_4OH, or NaOH, like aluminum.

METALS OF THE IRON GROUP.

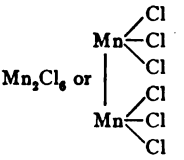
The metals, *iron, cobalt, nickel, manganese, chromium and zinc,* form sulphides (except chromium) which are insoluble in water but soluble in dilute acids, and are precipitated from solution by ammonium sulphide. Their oxides, hydroxides, carbonates, phosphates and sulphides are insoluble.

These metals decompose water at a red heat and dissolve readily in dilute sulphuric or hydrochloric acid, replacing the hydrogen.

Many of them form both basic and acid oxides, showing the properties of metals, on the one hand, and of non-metals on the other. In the compounds in which they enter as bases most of them are bivalent in one class of salts, and apparently trivalent but probably quadrivalent in another, thus:



Manganous chloride



Manganic chloride

In some other compounds they are sexivalent. Zinc is bivalent usually.

IRON (Ferrum).

Symbol, Fe. Atomic Weight, 55. Valence, II., IV., and VI.

History. Known to the ancient Egyptians and Assyrians. First employed as malleable iron, made by smelting ores with charcoal. Steel was described by Homer, and known to the ancient Greeks; the Chalybes, who lived on the shores of the Black Sea, were engaged in its manufacture.

Occurrence in Nature. Iron occurs native in meteorites, which consist chiefly of metallic iron with some nickel. The metal is usually found in combination, and is widely distributed in the soil as the oxide, imparting a reddish-brown color. It occurs as *ferric oxide,* or *haematite,* Fe_2O_3; *ferrous ferric oxide,* or *magnetic iron ore,* $FeO.Fe_2O_3$; *ferrous carbonate, or spathic iron ore,* $FeCO_3$; *ferric sulphide,* or *iron pyrites,* FeS_2. Iron occurs in plants in the chlorophyll, and in animals in the hæmoglobin. It is found in chalybeate mineral waters as ferrous sulphate and carbonate.

Preparation. By heating the oxides or carbonate with coke and limestone in large conical furnaces, at the base of which a blast of hot air is forced in. The iron ore and coke are fed into the furnace from the top in alternating layers, and by incomplete combustion in a layer of coke carbon monoxide is formed, this coming in contact with the iron ore removes oxygen and liberates the metal, forming carbon dioxide. The dioxide reaching another layer of heated coke again forms carbon monoxide, and a repetition of these changes continues to the top

of the furnace. The limestone with silicon of the ore forms slag, or silicate of calcium, which serves to protect the liberated metal. Molten iron and slag separate at the base of the furnace by a difference in specific gravity, iron being drawn off at the lower level.

Iron formed in this way is known as *pig, or cast iron,* and contains from 3 to 6 per cent. of carbon, besides some silicon and phosphorus; sometimes small percentages of other metals.

Wrought Iron, the purest commercial form, contains from .2 to .6 per cent. of carbon—official as iron wire.

Steel, intermediate in composition between the two varieties, contains .16 to 2 per cent. of carbon.

Carbon is removed from the cast iron by heating in an oxidizing flame. Steel can be made from cast iron by partial removal of carbon, or by mixing cast iron and wrought iron in proper proportions.

Properties. A gray metal, hard and tenacious. When heated it becomes soft, malleable and ductile, melting at 1150° to 1500°. Specific gravity about 7.7.

Iron is not much affected by dry air but easily oxidized when moisture is present. It forms two series of salts, ferrous and ferric, being bivalent in the former, and apparently trivalent in the latter. Compounds in which iron acts like a non-metal are known in the form of ferrates, where the metal is sexivalent.

Ferrum Reductum, Reduced Iron, *Iron by hydrogen.* A preparation of metallic iron in a fine state of subdivision.

Prepared by passing dry hydrogen gas over heated ferric oxide:

$$Fe_2O_3 + 3H_2 = 3H_2O + Fe_2.$$

Properties. A fine, dark-gray powder; odorless, insoluble in water; containing not less than 90 per cent. of metallic iron. It is easily oxidized by exposure. Used in medicine in form of pills.

Halogen Salts of Iron.

Ferrous Chloride, *Protochloride of iron,* $FeCl_2$. *Made* by dissolving iron in hydrochloric acid, and may be crystallized from this solution in green, deliquescent prisms.

$$Fe + 2HCl = FeCl_2 + H_2.$$

Ferric Chloride, *Sesqui-chloride, or perchloride of iron,* $Fe_2Cl_6.12H_2O$. *Prepared* by boiling a solution of ferrous chloride with hydrochloric and nitric acids:

$$6FeCl_2 + 2HNO_3 + 6HCl = 3Fe_2Cl_6 + 4H_2O + 2NO.$$

By evaporating the solution crystals may be obtained.

Properties. Orange-yellow, crystalline masses; deliquescent; soluble in water and in alcohol; acid reaction; styptic taste. Aqueous solution containing 29 per cent. of the anhydrous salt, is the official *Liquor Ferri Chloridi.* The tincture of chloride of iron, made by adding 35 parts of the above solution to 65 parts of alcohol, and allowed to stand for three months; the iron is thus partly reduced to ferrous state.

Ferrous Iodide, FeI_2. *Prepared* by warming a mixture of iodine, iron filings and water. Easily oxidized with liberation of iodine. The solution mixed with sugar of milk, and evaporated to dryness, constitutes *saccharated iodide of iron. Syrup of iodide of iron* is a solution of ferrous iodide and sugar. Ferric iodide does not exist at ordinary temperature of air.

Ferrous Bromide, $FeBr_2$. *Prepared* like ferrous iodide. Occurs in bluish-green crystalline tablets, with $6H_2O$. *Ferric Bromide,* Fe_2Br_6, obtained in dark-red crystals by direct union of the elements.

Iron Sulphur Compounds.

Ferrous Sulphide, FeS. *Made* by fusing together sulphur and iron. Occurs in dark-gray masses, metallic appearance; insoluble in water, soluble in acids with escape of H_2S. Largely used for making hydrogen sulphide as a reagent.

Ferric Sulphide, FeS_2. Occurs in nature as iron pyrites, and is largely used for making sulphuric acid and ferrous sulphate by roasting.

Oxygen Salts of Iron.

Ferrous Oxide, FeO, may be obtained by reducing the ferric oxide by the action of carbon monoxide, or hydrogen, but it is very unstable and rapidly absorbs oxygen from the air.

Ferrous Hydroxide, $Fe(OH)_2$, is formed by adding an alkaline hydroxide to a ferrous salt. It is a greenish-white powder, and rapidly absorbs oxygen to form brown ferric hydroxide:

$$FeSO_4 + 2NH_4OH = Fe(OH)_2 + (NH_4)_2SO_4.$$

$$2Fe(OH)_2 + O + H_2O = Fe_2(OH)_6.$$

Ferric Oxide, Fe_2O_3. Occurs in nature as hæmatite. *Prepared* by heating ferric hydroxide to expel water:

$$Fe_2(OH)_6 = Fe_2O_3 + 3H_2O.$$

Properties. A reddish-brown powder, used in the arts for polishing and as a pigment. A feeble base.

Ferric Hydroxide, Ferric Hydrate, *Hydrated oxide of iron, per- or sesqui-oxide of iron, red oxide of iron,* $Fe_2(OH)_6$.

Prepared by adding ammonia water to solution of ferric salt as a reddish-brown, gelatinous precipitate:

$$Fe_2(SO_4)_3 + 6NH_4OH = Fe_2(OH)_6 + 3(NH_4)_2SO_4.$$

Properties. A reddish-brown, insoluble powder. When freshly precipitated, used as an antidote in arsenic poisoning. Hydrated oxide of iron is used for this purpose, and is extemporaneously prepared by adding milk of magnesia to solution of ferric sulphate.

Ferrous-ferric Oxide, $FeO.Fe_2O_3$, occurs in nature as *magnetic iron ore, or loadstone.* It is formed when iron is burned in oxygen, or when steam is passed over red-hot iron. In

properties, it is a black solid, of metallic lustre, possessing magnetic power.

Ferrates. When potassium nitrate is fused with iron filings, a red mass containing potassium ferrate, K_2FeO_4, is formed, in which iron takes the part of a non-metal. The acid, H_2FeO_4, has not been separated, nor has the anhydride, FeO_3, iron trioxide. Iron has the valence of six in this compound.

Ferrous Sulphate, *Copperas, Green vitriol,* $FeSO_4.7H_2O$.

Prepared by dissolving iron in dilute sulphuric acid and crystallizing:

$$Fe + H_2SO_4 = FeSO_4 + H_2,$$

or by carefully roasting the native sulphide:

$$FeS_2 + 3O_2 = FeSO_4 + SO_2.$$

Properties. Large, bluish-green, prismatic crystals; efflorescent and absorbing oxygen to form some ferric sulphate when exposed to air; soluble in water, insoluble in alcohol. The *dried ferrous sulphate* formed as a white powder by heating carefully to 100° to expel four molecules of water. *Granulated ferrous sulphate* is formed as a granular powder by adding alcohol to aqueous solution of ferrous sulphate and drying the precipitate.

Ferric Sulphate, $Fe_2(SO_4)_3$. *Prepared* by boiling a solution of ferrous sulphate with sulphuric and nitric acids:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

The solution is known as *Solution of Tersulphate of Iron, Solution of Ferric Sulphate;* a reddish-brown liquid. By evaporating the liquid the salt may be obtained as a white mass. Forms alums with alkali sulphates. *Iron Ammonium Alum,* a pale, violet-colored, soluble salt.

Solution of Ferric Subsulphate, *Monsel's Solution.*

Prepared like the above salt except that the amount of sulphuric acid used is insufficient to form the normal salt.

Properties. A red liquid, miscible with water and alcohol, and powerfully astringent. (It is said to have the composition, $Fe_2(SO_4)_3.5Fe_2O_3.H_2O$.)

Ferrous Carbonate, $FeCO_3$. Occurs in nature as *spathic iron ore.*

Prepared by adding sodium carbonate to solution of ferrous sulphate:

$$FeSO_4 + Na_2CO_3 = FeCO_3 + Na_2SO_4.$$

The carbonate precipitates as a white powder, which rapidly turns dark by oxidation to ferric hydroxide. It is insoluble in water, slightly soluble in water containing CO_2. This salt, mixed with sugar to prevent oxidation, is used as *saccharated carbonate of iron. Ferric carbonate* is not known.

Ferric Nitrate, $Fe_2(NO_3)_6$. Formed by dissolving iron in nitric acid. It forms colorless, deliquescent, soluble, cubical crystals. A six per cent. solution is official. *Ferrous nitrate* is not known.

Ferrous Phosphate, $Fe_3(PO_4)_2.8H_2O$. Occurs in nature in the blue mineral *vivianite.*

Obtained as a precipitate by the action of sodium phosphate on ferrous sulphate, in presence of sodium acetate.

Properties. A slate-colored powder, turning dark by absorption of oxygen:

$$3FeSO_4 + 2Na_2HPO_4 = Fe_3(PO_4)_2 + 2Na_2SO_4 + H_2SO_4.$$

Ferric Phosphate, $Fe_2(PO_4)_2$, may be obtained as a white precipitate by adding sodium phosphate to solution of ferric chloride.

$$2Na_2HPO_4 + Fe_2Cl_6 = Fe_2(PO_4)_2 + 4NaCl + 2HCl.$$

Ferric Hypophosphite, $Fe_2(H_2PO_2)_6$. *Prepared* by dissolving ferric hydroxide in hypophosphorous acid, and crystallizing. A grayish powder, nearly insoluble in water.

Dialyzed Iron is *prepared* by adding ammonia water to solu-

tion of ferric chloride as long as the precipitate formed is redissolved on shaking, and placing the mixture in a dialyzer upon water. The water is renewed from time to time until all ammonium chloride passes out.

Properties. A dark, reddish-brown, odorless liquid, without the styptic taste and astringent properties of other iron compounds. Contains about five per cent. of ferric hydroxide and some ferric chloride. Is easily coagulated by acids, alkalies, and some salts.

Tests for Iron.

1. Ferrous compounds are converted into ferric by heating with nitric acid, and this is necessary for their complete precipitation.

2. Iron salts are precipitated black by ammonium sulphide.

3. Alkaline hydroxides give with ferrous salts a white precipitate, soon turning dark; with ferric salts, a reddish-brown gelatinous precipitate.

4. Alkaline carbonates give with ferrous salts a white precipitate, soon turning dark; with ferric salts, a reddish-brown precipitate and escape of CO_2.

5. Potassium ferrocyanide gives with ferrous salts a light-colored precipitate, soon turning light-blue; with ferric salts a dark-blue precipitate. (Prussian blue, $Fe_43Fe(CN)_6$.)

6. Potassium ferricyanide gives with ferrous salts a deep-blue precipitate (Turnbull's blue, $Fe_32Fe(CN)_6$); with ferric salts an olive green, or greenish-brown coloration, and no precipitate.

7. Potassium sulphocyanate gives with pure ferrous salts no change; with ferric salts a deep-red color.

8. Tannic acid gives no precipitate with a pure ferrous salt; with ferric salts it gives a greenish-black precipitate.

MANGANESE.

Symbol, Mn. Atomic Weight, 55. Valence, II. and IV.

Occurrence in Nature. As black oxide or pyrolusite,

MnO_2; and as sesquioxide, Mn_2O_3. In small quantities with other minerals.

Preparation. By heating the carbonate, or the above oxides with charcoal (C).

Properties. It resembles iron in its properties; is darker in color, harder and more easily oxidized; sp. gr. 7.2; decomposes boiling water. It forms both basic and acid oxides, with their corresponding salts.

Basic Oxides. The basic oxides of manganese form two classes of manganese salts with acids, *i. e., manganous compounds,* in which the metal is bivalent and strongly basic; and *manganic compounds,* in which the metal is apparently trivalent, but is really quadrivalent, like iron, and feebly basic. These basic oxides are:

Manganous Oxide,	MnO.
Manganous-Manganic Oxide,	$MnO.Mn_2O_3$.
Manganic Oxide,	Mn_2O_3.
Manganese Dioxide,	MnO_2.

Manganous Oxide. MnO.

Prepared by heating the carbonate.

Properties. A greenish-gray insoluble powder, strongly basic, forming salts with acids, which usually have a delicate rose color.

Manganic Oxide, Mn_2O_3. *Prepared* by heating the above oxide in a current of oxygen gas.

Properties. A black insoluble powder.

Manganese Dioxide, *Binoxide of Manganese, Black Oxide of Manganese,* MnO_2. Most important compound of manganese.

Occurs in nature as pyrolusite.

May be prepared by heating the nitrate.

Properties. A dark grayish-black, metallic-looking mineral, of crystalline structure. It gives up oxygen when heated. It is used for preparation of chlorine and oxygen, and also in medicine.

Manganous Sulphate, $MnSO_4$.

Prepared by dissolving the dioxide in sulphuric acid,

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O,$$

evaporating to dryness and igniting the residue, to decompose any ferrous sulphate that might be present, washing the residue with water, and crystallizing from the resulting solution.

Properties. A pale rose-colored solid, isomorphous with the sulphate of zinc, deliquescent and soluble in water.

Manganic Sulphate, $Mn_2(SO_4)_3$.

Prepared by action of H_2SO_4 on manganic oxide.

Occurs as dark green powder. Solutions red color. Forms alums, $K_2SO_4Mn_2(SO_4)_3.24H_2O$.

Manganous Chloride, $MnCl_2$.

Prepared by dissolving manganese dioxide in hydrochloric acid, evaporating to dryness and heating to dull redness, to decompose any iron salt present, washing the mass with water and crystallizing.

Properties. Rose-colored, soluble, deliquescent crystals.

Manganic Chloride, Mn_2Cl_6, is made by dissolving manganic oxide in cold hydrochloric acid. Easily decomposed to dichloride by heat. Never been separated pure.

The acid oxides of manganese are not known in the separate state, but only in combination.

Manganic Anhydride, $MnO_3 + H_2O = H_2MnO_4$, or *manganic acid.*

Permanganic Anhydride, $Mn_2O_7 + H_2O = H_2Mn_2O_8 = 2HMnO_4$, or *Permanganic acid.*

Permanganic Acid, $HMnO_4$, can be obtained in solution by electrolysis of a solution of potassium permanganate.

Potassium Manganate, K_2MnO_4.

Prepared by heating together manganese dioxide, potassium carbonate and potassium chlorate. The manganese is converted into manganic acid, which combines with the potassium present:

$$3MnO_2 + 3K_2CO_3 + KClO_3 = 3K_2MnO_4 + KCl + 3CO_2.$$

The manganate may be washed out and crystallized as a green soluble salt.

Potassium Permanganate, $KMnO_4$. *Prepared* by dissolving the manganate in acidulated water (or much water), when it is obtained as a violet-colored solution, with precipitation of manganese dioxide:

$$3K_2MnO_4 + 2H_2SO_4 = MnO_2 + 2K_2SO_4 + 2KMnO_4 + 2H_2O.$$

Properties. From the solution it may be crystallized in slender prismatic crystals of dark purple color, soluble in water. It is a strong oxidizing agent. It is used largely in medicine as a disinfectant.

Tests for Manganese.

1. Ammonium Sulphide gives a pink precipitate, soluble in acetic and mineral acids.

2. Ammonium, or Sodium Hydroxide gives a white precipitate which darkens by absorption of oxygen.

3. Potassium, or Sodium Carbonate gives a white precipitate.

4. Manganese Compounds heated on platinum foil with potassium carbonate and chlorate give a bluish-green mass, which, when dissolved in acidulated water, forms a violet-colored solution.

5. Violet color is imparted to the borax bead.

CHROMIUM.

Symbol, Cr. Atomic Weight, 52. Valence, II. and IV.

Occurrence in Nature. As chromite, or chrome iron ore, $FeOCr_2O_3$, which is similar in chemical structure to magnetic iron ore. The name signifies color, on account of the beautifully-colored compounds.

Preparation. By heating the oxide with charcoal to a high temperature.

Properties. Gray, metallic, crystalline powder; sp. gr. 6.8; very hard. Chromium forms both basic and acid oxides,

and three series of salts, *i. e., chromous* and *chromic* compounds, in which chromium takes the part of a base, and the salts of *chromic acid,* in which chromium exhibits acid properties.

The basic oxides:

Chromous oxide, CrO.

Chromic oxide, Cr_2O_3.

Chromous Oxide is not known in the anhydrous state. Is formed by adding potassium hydroxide to solution of chromous chloride—in the hydrated state $Cr(OH)_2$—as a brown precipitate, which is rapidly oxidized in chromic oxide. It is a strong base.

Chromic Oxide, *Sesquioxide of Chromium,* may be *prepared* by heating potassium dichromate with sulphur:

$$K_2Cr_2O_7 + S = K_2SO_4 + Cr_2O_3,$$

washing the resulting mass with water, when the oxide is left as a green powder, insoluble in water. It combines with acids to form salts, and is used in making green glass. It is known in commerce as *chrome green.*

Chromic Hydroxide, $Cr_2(OH)_6$.

Preparation. By adding solution of ammonium hydroxide to solution of chromic chloride, or other salt of chromium:

$$Cr_2Cl_6 + 6NH_4OH = Cr_2(OH)_6 + 6NH_4Cl.$$

Properties. A bluish-green, gelatinous, insoluble powder. By dissolving the hydroxide in different acids, the salts of chromium are formed.

Potassium chromium sulphate, and ammonium chromium sulphate are double salts having the chemical character of alums.

The acid oxide of Chromium:

Chromium Trioxide, *Chromic Acid, Chromic Anhydride,* CrO_3.

Preparation. By adding sulphuric acid to a concentrated

solution of potassium bichromate, the trioxide separates in needle-shaped crystals:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3.$$

Properties. Long, red, needle-shaped crystals; deliquescent when exposed to the air, and freely soluble in water. It is strongly corrosive, a powerful oxidizing agent, and when heated gives up oxygen. Its solution in water has acid properties.

The formation of chromic and di-chromic acids may be explained by the following equations:

$$CrO_3 + H_2O = H_2CrO_4, \text{ Chromic Acid.}$$

$$2CrO_3 + H_2O = H_2Cr_2O_7, \text{ Di-Chromic Acid.}$$

Chromic Acid, H_2CrO_4; made by adding water to CrO_3 and heating to 100°, decanting, and clear liquid cooled to 0°, when the acid separates in red, deliquescent crystals.

Potassium Bichromate, *Potassium Dichromate,* $K_2Cr_2O_7$. *Preparation.* By heating in an oxidizing furnace chrome iron ore and potassium carbonate. Chromic acid is thereby formed, which combines with the potassium, forming *potassium chromate:*

$$2(FeOCr_2O_3) + 4K_2CO_3 + 7O = Fe_2O_3 + 4CO_2 + 4K_2CrO_4.$$

The resulting mass is washed with water, which dissolves out the chromate. *Potassium chromate, or yellow chromate of potash,* can be crystallized from solution by evaporation; it is a yellow, crystalline solid, freely soluble in water. Upon acidifying the solution of potassium chromate with sulphuric acid and heating, potassium bichromate is formed:

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + H_2O + K_2Cr_2O_7.$$

Properties. Large, red crystals, soluble in ten parts water. When heated it fuses, and finally gives off oxygen. A strong

oxidizing agent. By the action of alkalies it is converted into potassium chromate:

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Tests for Chromium.

1. *Compounds* of *chromium,* when heated on platinum foil with potassium chlorate and carbonate, give a yellow color.

2. Green color to borax bead.

In salts of *chromium,* as, Cr_2Cl_6:

3. Ammonium hydroxide, or sulphide, gives a green precipitate of chromic hydroxide.

4. Potassium, or sodium hydroxide, gives the same precipitate, soluble in excess,

In chromates, as, K_2CrO_4:

5. Hydrogen sulphide in acid solution gives a green color.

6. Solutions of lead salts give yellow precipitate soluble in HCl and NaOH; insoluble in acetic acid.

7. Solution barium chloride gives yellow precipitate.

8. Silver and mercurous nitrate give red precipitate in neutral solutions.

COBALT.

Symbol, Co. Atomic Weight, 58. Quantivalence, II. and IV.

Occurrence in Nature. As sulphide, as arsenide and arsenate, and as cobaltic oxide.

Preparation. By heating cobaltous oxide with carbon, or in a current of hydrogen.

Properties. A reddish-white, lustrous metal; very tenacious and difficult to fuse; specific gravity, 8.9; permanent in air, not affected by water. Nitric acid dissolves it readily, but it is not much affected by hydrochloric or sulphuric acids. Cobaltous compounds are the ones it usually forms, and they are isomorphous with ferrous salts. Anhydrous salts have a blue color; hydrous salts, a reddish color.

Cobaltous Chloride, $CoCl_2$. Made by dissolving cobaltous oxide in hydrochloric acid and crystallizing.

Properties. Red, prismatic crystals containing six molecules of water. When heated it becomes anhydrous and turns blue.

Cobaltous Nitrate. Made by dissolving the oxide or metal in nitric acid. Forms red, deliquescent prisms; soluble.

Tests for Cobalt.

1. Ammonium sulphide gives a black precipitate of sulphide.

2. KOH, or NaOH, gives a blue precipitate, which turns pink on boiling.

3. NH_4OH gives blue precipitate soluble in excess.

Sodium Cobaltic Nitrite formed by action of sodium nitrite on solution of cobaltous nitrate—$Co_2(NO_3)_4.6NaNO_2$. Used in solution as test for potassium, giving yellow precipitate.

NICKEL.

Symbol, Ni. Atomic Weight, 58. Valence, II. and IV.

Occurs free in meteorites; in combination as sulphide, arsenide and silicate, frequently with cobalt. The pure metal obtained by heating oxide or carbonate in hydrogen.

Properties. Silver-white, lustrous, tenacious, specific gravity, 9.1; not affected by air; not easily dissolved in HCl or H_2SO_4, but easily in HNO_3. Most of its salts of the ous form. Used with copper and zinc in German silver, nickel-steel armor plate, nickel plate.

Nickelous Sulphate, $NiSO_4.7H_2O$. Made by dissolving oxide in H_2SO_4. Forms green crysals, soluble in water, isomorphous with magnesium sulphate.

Tests for Nickel.

1. $(NH_4)_2S$: black precipitate.

2. Sodium or potassium hydroxide gives a green precipitate, unaltered by boiling.

3. Ammonium hydroxide gives a green precipitate, soluble in excess.

ZINC.

Symbol, Zn. Atomic Weight, 65. Valence, II.

Occurrence in Nature. Zinc is somewhat abundant, occurring in nature in combination as the carbonate, the silicate and sulphide, or zinc blend; sometimes as red oxide, or zincite.

Preparation. By heating the carbonate or oxide with charcoal in clay tubes, when the liberated metal distills:

$$ZnO + C = Zn + CO.$$

Properties. A bluish-white metal; very little affected by the air. It has a crystalline structure, and is brittle at ordinary temperatures. Its specific gravity is 7.2. Zinc, when heated

to 120° or 150°, becomes malleable, and may be beaten into leaves or drawn out into wire; it retains these properties when cooled. At 200° it becomes brittle again. It fuses at 410° and volatilizes at 1000°, if air be excluded. With access of air it burns to zinc oxide, giving a bluish-white light. Owing to its permanence in the air, zinc is much used in the metallic state in the form of sheet zinc and for galvanizing iron. It is used also in many valuable alloys, as brass and German silver.

Zinc forms but one class of salts, in which it is bivalent; nearly all of its salts are white.

Zinc Oxide, *Zinc White, Flores Zinci, Lana Philosophica,* ZnO. Prepared by heating the precipitated basic carbonate, when water and carbon dioxide are driven off and the oxide remains. Also by burning the metal. *Properties:* An amorphous, insoluble, tasteless powder. It turns yellow when heated, and resumes its white color upon cooling. Found in nature as zincite, colored by impurities.

Zinc Hydroxide, $Zn(OH)_2$. *Prepared* by adding solution of an alkaline hydroxide to solution of a salt of zinc, as a white amorphous precipitate, soluble in excess of alkali.

Zinc Chloride, $ZnCl_2$. *Preparation.* By heating zinc in a stream of chlorine, or by distilling a mixture of zinc sulphate and calcium chloride. Usually prepared by dissolving zinc or zinc carbonate, in hydrochloric acid, and evaporating the solution to dryness.

Properties. A white, granular, crystalline powder, or a white opaque mass. It is deliquescent, soluble in water and alcohol, fuses at 115°, and volatilizes with partial decomposition at 680°. Zinc chloride forms double compounds with ammonia ($ZnCl_2NH_3$) and with potassium chloride; it combines with albuminoid bodies, and acts as a caustic upon the tissues.

Zinc Bromide, $ZnBr_2$, is analogous to the chloride in method of preparation and properties.

Zinc Iodide, ZnI_2. *Prepared* by heating the two elements together in water, and evaporating to dryness.

Properties. Like those of the chloride.

Zinc Carbonate, *Precipitated carbonate of zinc,* $2ZnCO_3 \cdot 3Zn(OH)_2$. *Preparation.* By boiling together solutions of zinc sulphate and sodium carbonate, collecting, washing and drying the precipitate:

$$5ZnSO_4 + 5Na_2CO_3 + 3H_2O = 2ZnCO_3.3Zn(OH)_2 + 5Na_2SO_4 + 3CO_2.$$

Properties. A white, impalpable, odorless, tasteless powder, insoluble in water, soluble in ammonia water and in acids.

Zinc Sulphate, *white vitriol,* $ZnSO_4$. *Preparation.* By gently roasting zinc blende, or by dissolving zinc in dilute sulphuric acid:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Properties. Small, colorless crystals, isomorphous with magnesium sulphate, containing 7 molecules water of crystallization, freely soluble in water.

Zinc Phosphide, Zn_3P_2. *Preparation.* By the action of phosphorus upon melted zinc.

Properties. A grayish-black, insoluble, crystalline solid, having a metallic appearance.

Toxicology. Salts of zinc act as acute irritant poisons, producing pain, nausea, vomiting and purging.

In case of poisoning, milk, albumen and tannic acid act as antidotes.

Tests for Zinc.

1. To solution of zinc salt add ammonium sulphide; a white precipitate of zinc sulphide is produced.

2. Add solution of potassium, sodium or ammonium hydroxide; a white precipitate of zinc hydroxide forms, soluble in excess. A similar precipitate forms with magnesium compounds, insoluble in excess of reagent.

3. Add solution of potassium ferrocyanide; a white precipitate of zinc ferrocyanide forms; magnesium forms no precipitate with this reagent.

4. Add solution of a carbonate, or phosphate, to neutral solution of zinc salt; a white precipitate forms.

Analytical Reactions.

Directions for analysis of an aqueous solution containing one or all of the metals Al, Fe, Co, Ni, Mn, Cr, and Zn.

To the solution add NH_4OH until a precipitate remains after shaking. Add NH_4Cl, $(NH_4)_2S$ in excess, heat, filter and wash the precipitate. The precipitate contains all the metals of this group as sulphide, except Cr and Al which exist in the precipitate as hydroxides. Stir the precipitate with dilute cold HCl. Filter and wash.

<table>
<tr><td>Precipitate.
Sulphides of Co, Ni.
Dissolve in nitrohydrochloric acid, evaporate nearly to dryness, add a few c. c. of water, and KNO_2, acidify with acetic acid, warm and allow to stand. A yellow precipitate of potassium cobaltic nitrite is formed, after several hours. Filter, add NaOH to the filtrate and warm. A green precipitate of $Ni(OH)_2$ is formed. To another portion of the filtrate add $(NH_4)_2S$; a black precipitate of NiS is formed.</td><td colspan="3">Filtrate.
Fe, Zn, Al, Cr, Mn.
Boil, to expel hydrogen sulphide and add excess of bromine water. Make alkaline with NaOH, boil and filter.</td></tr>
<tr><td></td><td>Precipitate.
Fe, Cr, Mn.
Divide into two portions and test as follows:
1. Dissolve in HCl and test for iron by adding $K_4Fe(CN)_6$. Blue color.
2. Dry and fuse on platinum foil with Na_2CO_3 and KNO_3. A green color indicates Mn.
Add water, boil, acidify with acetic acid and add lead acetate. A yellow precipitate, if Cr be present.</td><td colspan="2">Filtrate.
Al, Zn.
Make slightly acid with HCl, add excess of NH_4OH and boil. Al is precipitated white. Filter.</td></tr>
<tr><td></td><td></td><td>Precipitate.
$Al_2(OH)_6$</td><td>Filtrate.
Zn.
Divide in two portions: 1. Add $(NH_4)_2S$; a white precipitate of ZnS forms. 2. Add $K_4Fe(CN)_6$ and a few drops of HCl; white precipitate of $Zn_2Fe(CN)_6$.</td></tr>
</table>

METALS OF THE LEAD GROUP.

The metals, *lead, copper, silver, bismuth, mercury and cadmium* constitute the metals of the lead group. They form sulphides which are insoluble in water, ammonium sulphide, or dilute mineral acids; they are, therefore, precipitated by hydrogen sulphide from acid solution, and by ammonium sulphide.

The metals of this group do not decompose water at any temperature, and are not dissolved by dilute hydrochloric or sulphuric acids.

Hot sulphuric acid, and nitric acid dissolve the metals to form salts, with replacement of the hydrogen and decomposition of part of the acid radical, as shown by the following equations:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

$$3Ag + 4HNO_3 = 3AgNO_3 + 2H_2O + NO.$$

The oxides, iodides, sulphides, phosphates and carbonates are insoluble; the chlorides and sulphates are soluble, with some exceptions.

LEAD (Plumbum).

Symbol, Pb. Atomic Weight, 205. Valence, II.

Occurrence in Nature. As sulphide frequently in company with silver, and as carbonate.

Preparation. Almost exclusively obtained from the sulphide, by roasting and heating with coke. Also prepared by roasting with access of air, stirring and mixing thoroughly, and further roasting without air; the chemical changes taking place when the lead ores are roasted with access of air, and the further changes occurring when the air is excluded, are shown in the following equations:

$$\left.\begin{array}{l} PbS + 3O = PbO + SO_2. \\ PbS + O_4 = PbSO_4. \end{array}\right\} \text{ with access of oxygen of air.}$$

$$\left.\begin{array}{l} PbS + 2PbO = Pb_3 + SO_2. \\ PbSO_4 + PbS = Pb_2 + 2SO_2. \end{array}\right\} \text{ without access of air.}$$

Properties. A bluish-white, soft metal, whose freshly-cut surface shows a bright appearance which soon tarnishes by exposure. The specific gravity of lead is 11.37; it fuses at 325°, and distills at a white heat; it burns to the oxide when highly heated in the air.

The metal is not much affected by hydrochloric or sulphuric acids on account of the formation of the sulphate or chloride on its surface which acts as a protective coating; it will dissolve in these acids when reduced to the form of a fine powder. Solutions of lead salts are precipitated by the presence of zinc, tin, or iron, the metal being deposited upon these metals in the form of fine crystals.

Lead is largely used in the metallic state in the manufacture of alloys, of chemical vessels and of lead pipes. Water containing air or nitrates is liable to become contaminated by passage through lead pipes, but water containing a small quantity of carbonates or sulphates forms an insoluble protective coating on the inner surface of the pipes.

Lead Oxide, PbO, is prepared by heating lead in a current of air, when the lead forms a yellow powder, called "massicot"; this, when heated, fuses to reddish-yellow scales of "litharge." Further heating of litharge in air results in the formation of a mixture of PbO and PbO_2, or "red lead," which is used as a pigment.

Lead oxide is used in making the salts of lead, *lead plaster,* paint and glass.

Lead Nitrate, $Pb(NO_3)_2$. *Preparation:* By dissolving the oxide in nitric acid, as shown in the equation:

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

Properties. A white, soluble salt; sweetish, astringent, metallic taste.

Basic Carbonate of Lead, White Lead, $2PbCO_3.Pb(OH)_2$.

Preparation. By boiling lead nitrate with the oxide, and precipitating by CO_2. Also prepared by action of vapors of acetic acid and carbon dioxide on lead.

Properties. White, insoluble powder; used with linseed oil in making paint.

Lead Iodide, PbI_2. *Preparation:* By mixing solutions of potassium iodide and lead nitrate, and filtering out the precipitate. The following equation shows the reaction:

$$Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3.$$

Properties. Heavy, yellow powder; insoluble in water, soluble in hot solution of ammonium chloride.

Lead Sulphate, $PbSO_4$, is prepared by adding a solution of sodium sulphate to a solution of lead nitrate, when the lead sulphate forms as a white precipitate, which is separated by filtration. The following equation represents the formation of this salt:

$$Pb(NO_3)_2 + Na_2SO_4 = 2NaNO_3 + PbSO_4.$$

Properties. A white, insoluble, tasteless powder.

Toxicology of Lead. Lead poisoning occurs in two forms, acute and chronic. *Acute lead poisoning* occurs from the ingestion of a soluble salt of lead, or of the finely divided metal. The chief symptoms are a sense of constriction in the throat and pharynx, abdominal pain, stiffness of the abdominal muscles, paralysis of the lower extremities, scanty urine, blueness of the gums and great prostration with convulsions. *The antidote* is diluted sulphuric acid, and magnesium sulphate. The stomach should be emptied.

Chronic Lead Poisoning occurs in those engaged in the manufacture or use of lead or its salts, or in those who drink water which has been contaminated with the metal. The chief symptoms are as follows: A blue line on the gums; pallor; emaciation; quick, feeble pulse; obstinate constipation; attacks of colic; paralysis of the extensor muscles of the fore-arm, or "wrist drop." The treatment consists in the use of saline purgatives, diluted sulphuric acid, followed by the use of potassium iodide and galvanism of the paralyzed muscles.

Tests for Lead.

1. Hydrogen sulphide, or ammonium sulphide gives black precipitate, insoluble in dilute hydrochloric acid or ammonium sulphide.

2. Sulphates give a white precipitate.

3. Potassium iodide gives a yellow precipitate, soluble in hot solution of ammonium chloride.

4. Potassium chromate gives a yellow precipitate.

5. Caustic potash gives a white precipitate, soluble in excess—plumbates, K_2PbO_3.

6. Ammonia water gives a white precipitate, insoluble in excess.

7. Dilute hydrochloric acid in cold, strong solutions of lead salts, gives white, granular precipitate, soluble in boiling water.

COPPER (Cuprum).

Symbol, Cu. Atomic Weight, 63. Valence, II.

Occurrence in Nature. Copper is found in nature as the sulphide, or *copper glance;* as the carbonate and hydroxide, in the green mineral, *malachite;* as the oxide; sometimes in the free state. The metal also occurs as copper and iron sulphide, Cu_2FeS_2, in *copper pyrites.*

Preparation. By heating the oxide or carbonate with carbon.

Properties. A red, soft, malleable, ductile metal. Specific gravity 8.9; fuses at 1054°; forms coating of copper carbonate in moist air; burns to black oxide when highly heated in air. The metal is not much affected by dilute sulphuric or hydrochloric acids; with strong sulphuric acid it forms copper sulphate, evolving sulphur dioxide; with nitric acid it forms copper nitrate with evolution of nitrogen dioxide. Zinc and iron precipitate copper from solution of its salts.

The metal is largely used in making alloys, copper vessels and wire.

Copper forms two classes of salts, cuprous and cupric compounds; it is univalent in the former and bivalent in the latter. The cuprous salts are very unstable, passing into the cupric form.

Cupric Oxide, *Black Oxide of Copper,* CuO. *Prepared* by heating copper in the air, by heating the nitrate, or carbonate, or by boiling the precipitated hydroxide.

Properties. A black, insoluble, amorphous powder. *Used* for preparing copper salts and for analyzing organic bodies.

Cuprous Oxide, Cu_2O. *Prepared* by boiling a solution of copper sulphate, potassium hydroxide and glucose, when it separates as a reddish-brown crystalline powder.

Cupric Sulphate, *Blue Vitriol, Bluestone,* $CuSO_4.5H_2O$. *Prepared* by carefully roasting cupric sulphide, or by dissolving cupric oxide in sulphuric acid, and crystallizing:

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

Properties. Large, transparent, blue, prismatic crystals; nauseous, metallic, astringent taste; soluble in water, insoluble in alcohol; becomes anhydrous at 200°.

Cupric Carbonate, $CuCO_3.Cu(OH)_2$. The normal salt not known, but cupric carbonate and hydroxide is precipitated from cupric solutions by adding sodium carbonate. Occurs as a bluish-green powder.

Cupric Chloride, $CuCl_2.2H_2O$. A green, deliquescent, soluble, crystalline salt.

Ammonio-Copper Compounds. Compounds of copper form double salts with ammonia in which the molecule of copper salt combines with two, four and sometimes six molecules of NH_3. When ammonia water is added to solution of cupric sulphate a deep-blue solution is formed, from which large, deep blue crystals may be obtained by evaporation, having the composition, $CuSO_4(NH_3)_4.H_2O$.

Toxicology of Copper. The salts of copper act as poisons. Culinary vessels, made of the metal, if allowed to oxidize by lack of cleanliness, will form copper salts with fruit and vegetable juices. The symptoms of poisoning by copper are those of an irritant poison; they are abdominal pain, vomiting, purging, great prostration and sometimes jaundice. The antidote is egg albumen, and demulcent drinks.

Tests for Copper.

1. Ammonium sulphide, or hydrogen sulphide, gives a black precipitate.

2. Sodium, or potassium hydroxide, gives a bluish precipitate which blackens upon boiling, forming cupric oxide.

3. Ammonia water causes a pale-blue precipitate which quickly dissolves, forming a deep-blue liquid.

4. Potassium ferrocyanide gives a chocolate-brown precipitate; not obtained in alkaline solution.

5. Cupric salts give blue borax bead; cuprous salts, red.

6. Alkaline carbonates give a pale-green precipitate.

7. A piece of bright iron wire in acidified solution of copper acquires a coating of metallic copper.

BISMUTH.

Symbol, Bi. Atomic Weight, 207. Valence, III and V.

Occurrence in Nature. Usually found in the free state disseminated in rocks. Sometimes as oxide, Bi_2O_3, or *bismuth ochre;* occasionally as sulphide, Bi_2S_3, or *bismuthite.*

Preparation. Made by mechanical means, by heating the ore in iron tubes inclined so as to allow the melted metal to run out into suitable vessels.

Properties. Isomorphous with arsenic and antimony. A brilliant grayish-white metal; hard, brittle, and may be easily reduced to powder. When melted it expands in solidifying. Specific gravity, 9.83; melts at 264°; permanent in the air; insoluble in hydrochloric acid, soluble in nitric and hot sulphuric acid. Frequently contains arsenic as an impurity, which

may be removed by heating with potassium nitrate and hydroxide.

The compounds show a tendency to decompose with water to form oxy- or sub-salts, in which the radical (BiO) behaves like a univalent atom. Used for preparation of its salts and in alloys.

Bismuth Trichloride, $BiCl_3$. Made by dissolving the metal in nitro-hydrochloric acid, evaporating to dryness and distilling the residue.

Properties. A white, deliquescent mass; fusible and volatile; soluble in alcohol; known as bismuth butter. By mixing the alcoholic solution with much water, forms a white insoluble crystalline powder of basic bismuth chloride, BiOCl.

Bismuth Sub-Iodide, or Oxy-Iodide, BiOI. *Prepared* by boiling together solutions of bismuth subnitrate in nitric acid, and potassium iodide in water, when the precipitate formed is washed and dried. It occurs as a brick-red insoluble powder, and is used as an antiseptic dressing, like iodoform.

Bismuthyl Nitrate, Bismuth Subnitrate, $(BiO)NO_3.H_2O$. *Preparation.* When metallic bismuth is dissolved in nitric acid, the normal nitrate forms, and may be obtained by crystallization from the solution in colorless, transparent crystals:

$$\underset{\text{Bismuth}}{Bi_2} + \underset{\text{Nitric acid}}{4HNO_3} = \underset{\text{Bismuth nitrate}}{2Bi(NO_3)_3} + \underset{\text{Water}}{2H_2O} + \underset{\text{Nitrogen dioxide}}{NO.}$$

If the solution of bismuth nitrate thus formed be poured into a large quantity of water, the subnitrate separates as a white powder, which may be washed and dried for use:

$$\underset{\text{Bismuth nitrate}}{Bi(NO_3)_3} + \underset{\text{Water}}{2H_2O} = \underset{\text{Bismuth subnitrate}}{(BiO)NO_3H_2O} + \underset{\text{Nitric acid}}{2HNO_3.}$$

Properties. A white powder, almost insoluble in water, insoluble in alcohol, soluble in nitric and hydrochloric acids. When heated to redness it gives off nitrous fumes, and leaves

a yellow residue of oxide, soluble in nitric or hydrochloric acid.

Uses. Largely used in medicine, and used in cosmetics under the name of flake white.

Bismuth Subcarbonate, Bismuthyl Carbonate, Basic Bismuth Carbonate, $(BiO)_2CO_3.H_2O$. (*Pearl white.*)

Preparation. By mixing a solution of sodium carbonate and solution of bismuth nitrate, collecting, washing and drying the precipitate:

$$\underset{\text{Bismuth nitrate}}{2Bi(NO_3)_3} + \underset{\text{Sodium carbonate}}{3Na_2CO_3} + \underset{\text{Water}}{H_2O} = \underset{\text{Sodium nitrate}}{6NaNO_3} + \underset{\text{Carbon dioxide}}{2CO_2} + \underset{\text{Bismuth subcarbonate}}{(BiO)_2CO_3H_2O}.$$

Properties. "A white or pale, yellowish-white powder," insoluble in water, soluble in nitric or hydrochloric acid with effervescence. When heated, water and carbon dioxide are driven off and the yellow oxide is left (Bi_2O_3). Used in medicine.

Tests for Bismuth.

1. Hydrogen sulphide or ammonium sulphide when added to solution of bismuth salt will produce a dark brown precipitate.

2. Solution of bismuth salt poured in much water gives a white precipitate of oxysalt.

3. Solution of hydroxides or carbonates of the alkalies give a white precipitate.

4. Solution of potassium iodide gives a brown precipitate, soluble in excess.

5. Solution of potassium dichromate gives a yellow precipitate.

6. *Dry reaction.* Bismuth or its compounds mixed with sulphur and potassium iodide, and heated on charcoal in blowpipe flame, give a red incrustation of bismuthyl iodide.

SILVER (Argentum).

Symbol, Ag. Atomic Weight, 107. Quantivalence, I.

History. Well known to the ancients. Called Luna by the alchemists.

Occurrence in Nature. Free, in masses, sometimes. In combination with chlorine, bromine, iodine, sulphur and arsenic. Occurs most abundantly as sulphide Ag_2S or silver glance; frequently found in company with lead as argentiferous galena. The native chloride is known as horn silver.

Preparation. The extraction of silver is accomplished in several different ways, only one of which need be mentioned. It is largely obtained from lead made from argentiferous galena by the Pattison process, which consists in melting the alloy and allowing it to cool slowly, when lead crystallizes first and is dipped out with a perforated ladle. The remaining alloy, rich in silver, is heated in a porous crucible in a current of air, which oxidizes the remaining lead and leaves metallic silver as a button in the bottom of the crucible.

Properties. A pure white, lustrous metal, taking a high polish. It is soft, ductile and malleable, and can be made into fine wire or foil; comes next to gold in this respect; can be beaten to leaf .00025 m.m. in thickness, and wire so fine that 180 metres weigh 0.1 gm. Thin films transmit green light. Specific gravity 10.5; melts at 940°; vaporized in oxy-hydrogen flame, vapor green. Not affected by oxygen, but absorbs twenty-two times its volume of oxygen when molten, which it gives up upon cooling; it is oxidized by ozone.

While silver is not affected by oxygen, it is readily tarnished by the presence of hydrogen sulphide, which turns it black. The metal is capable of existing in several allotropic forms, all of which have decided color, and are formed by precipitating the metal from solution by the action of reducing agents.

Silver unites directly with the halogens to form salts. It dissolves in hot, strong sulphuric acid.

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2.$$

It is not much affected by hydrochloric acid or by dilute sulphuric acid in the cold. It is very soluble in nitric acid:

$$3Ag + 4HNO_3 = 3AgNO_3 + 2H_2O + NO.$$

Silver is too soft for use in the arts pure; generally alloyed with 10 per cent. of copper.

Chemically Pure Silver is prepared by dissolving in nitric acid, precipitating the solution with sodium chloride, and heating with sodium carbonate:

$$2AgCl + Na_2CO_3 = 2NaCl + CO_2 + O + Ag_2.$$

Silver Chloride, AgCl, occurs in nature as horn silver. *Prepared* by adding HCl to solution of silver nitrate. It is a white insoluble powder, turning dark by exposure; soluble in ammonia water.

Silver Nitrate, $AgNO_3$. *Preparation.* By dissolving pure silver in nitric acid, evaporating to dryness and heating to expel remaining nitric acid. The residue is redissolved in water and crystallized.

Properties. White, transparent, shining, tabular crystals; decomposed by light and organic matter; soluble in water and alcohol. In making a solution of silver nitrate, pure distilled water is necessary, in order to prevent decomposition of the salt. This salt acts as a caustic upon the tissues of the body, being decomposed by them, with liberation of nitric acid and finely divided metallic silver. *Luna caustic* is silver nitrate, containing four per cent. of HCl, moulded into pencils for use as a caustic. *Mitigated caustic* contains one part $AgNO_3$ and two parts KNO_3.

Silver Oxide, Ag_2O. *Preparation.* By adding solution caustic potash to solution silver nitrate, collecting, washing and drying the precipitate:

$$2AgNO_3 + 2KOH = 2KNO_3 + H_2O + Ag_2O.$$

Properties. Dark-brown, insoluble powder. A strong base, easily reduced by oxidizable bodies.

Silver Iodide, AgI. Made by adding solution potassium iodide to solution silver nitrate, collecting, washing and drying the precipitate.

Properties. Insoluble, yellow powder.

Poisoning by silver occurs from ingestion of the soluble salts of the metal; they act as corrosive irritants. The antidote is sodium chloride, to form the insoluble silver chloride; and demulcent drinks, to allay the irritation.

Tests for Silver.

1. Hydrogen sulphide, or ammonium sulphide, gives brown precipitate.
2. Hydrochloric acid, or solution of a chloride, gives a white curdy precipitate, soluble in ammonia water.
3. Alkali hydroxides give brown silver oxide as a precipitate.
4. Solution of potassium iodide gives a pale yellow precipitate.
5. Potassium chromate gives a brick red precipitate.

MERCURY (Hydrargyrum, Quicksilver).

Symbol, Hg. Atomic Weight, 199. Valence, II.

History. Well known to the ancients, and attracted much attention on account of its peculiar physical properties. Mentioned in the writings of Aristotle 400 B. C., and it was described by another writer as liquid silver.

Occurrence in Nature. Found in the free state amalgamated with gold and silver sometimes; more frequently, disseminated through its ores in small globules. The most abundant ore is the sulphide, or cinnabar, HgS. Found in Austria, Spain, Nevada, Utah, California, Mexico, New Mexico, New South Wales, China and Japan.

Preparation. Prepared by heating the ore in a current of air above 360°, when the sulphur is oxidized and the metal passes off as a vapor. The vapor of mercury passes through a series of stone chambers and is collected under water; this reaction is shown in the equation:

$$HgS + O_2 = Hg + SO_2.$$

Sometimes the ores are heated with lime, as shown in the equation:

$$4HgS + 4CaO = CaSO_4 + 3CaS + 4Hg.$$

The metal is sent into commerce in iron bottles containing about eighty pounds each, and contains mechanical impurities besides lead, tin, silver, bismuth, copper or zinc. It is purified by pressing through chamois skin and carefully distilling from iron retorts. Metallic impurities are further removed by the action of dilute nitric acid.

Properties. Mercury is a silvery-white liquid, having a bright metallic lustre.

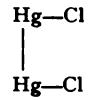
At a temperature of — 39.38° it becomes a malleable, ductile crystalline solid, and contracts in volume upon solidifying. In very thin layers it transmits a violet-blue light; its specific gravity is 13.56.

Mercury volatilizes slowly at ordinary temperatures, and boils at 357.25°, giving a colorless, very poisonous vapor. It is insoluble in the usual solvents; is not dissolved by hydrochloric acid, or cold sulphuric. When heated with strong sulphuric acid it dissolves, forming the sulphate with liberation of sulphur dioxide; it is easily dissolved by nitric acid, with escape of nitrogen dioxide; it unites directly with Cl, Br and I.

The pure metal is not affected by the oxygen of the air, but when other metals are present it becomes gray from thin oxidation. A globule should not leave a streak when rolled over paper, showing absence of lead and tin.

The molecular and atomic weight of mercury are the same, showing that its molecule contains but one atom.

Mercury forms two classes of compounds; the mercurous, in which it is apparently univalent, and the mercuric, in which it is bivalent. In mercurous salts two atoms of mercury exert the quantivalence of two, one unit of attraction in each atom being devoted to its fellow. This molecular structure is found in mercurous chloride, Hg_2Cl_2, and is clearly shown in the graphic formula for this compound, thus:



Uses. For making scientific instruments, for silvering mirrors, for amalgams, and for preparation of compounds.

Used in medicine in the metallic state in fine state of subdivision in *blue mass, mercury with chalk, mercurial plaster and mercurial, or blue ointment.*

COMPOUNDS OF MERCURY.

Mercurous Chloride, Calomel, *Subchloride of Mercury, Protochloride of Mercury, Submuriate of Mercury,* Hg_2Cl_2. Found native and impure in horn-quicksilver.

Preparation. Can be made by adding hydrochloric acid to solution of mercurous nitrate when it forms as a granular powder, or by triturating mercuric chloride with mercury and subliming. Usually prepared by triturating mercuric sulphate with mercury, mixing with sodium chloride, and subliming:

$$HgSO_4 + Hg = Hg_2SO_4.$$

$$Hg_2SO_4 + 2NaCl = Na_2SO_4 + Hg_2Cl_2.$$

It is then washed with hot water and dried.

Properties. White, amorphous, insoluble, odorless, tasteless powder. Volatilizes without melting. By oxidation it has a

tendency to pass into the mercuric salt. Calomel is decomposed by the action of strong mineral acids, alkaline hydroxides, carbonates, bromides and iodides, and is therefore incompatible with these compounds. Calomel is often prescribed with sugar or sodium bicarbonate to prevent oxidation.

Mercuric Chloride, *Bichloride, Corrosive Sublimate, Perchloride, Sesquichloride, Corrosive Chloride of Mercury,* $HgCl_2$.

Preparation. By subliming a mixture of mercuric sulphate and sodium chloride:

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2.$$

By dissolving mercuric oxide in hydrochloric acid:

$$HgO + 2HCl = H_2O + HgCl_2.$$

Properties. White, translucent, crystalline masses, forming a white granular powder. Odorless, sharp metallic taste.

Soluble in sixteen parts water, two parts hot water, three parts alcohol, fourteen parts glycerine, four parts ether. It melts and volatilizes by heat, and its solution has an acid reaction. Shows a tendency to form basic chlorides, and double chlorides with the alkali metals. This salt is largely used as an antiseptic. It acts as a corrosive irritant poison, and the antidote is egg albumen.

Mercurous Iodide, *Protoiodide, Subiodide, Green Iodide, Yellow Iodide,* Hg_2I_2. Can be made by rubbing mercury, alcohol and iodine together in a mortar, when it has a green color.

Usually *prepared* by adding solution of potassium iodide to solution of mercurous nitrate, collecting the precipitate, washing with alcohol, and drying with exclusion of light:

$$Hg_2(NO_3)_2 + 2KI = 2KNO_3 + Hg_2I_2.$$

Properties. A yellow, amorphous, odorless, tasteless, insoluble powder. By exposure to light it becomes darker, form-

ing mercury and mercuric iodide; by heat, it melts and sublimes.

Mercuric Iodide, *Biniodide, Red Iodide,* HgI_2. Can be made by direct union of the elements. Usually *made* by adding solution of potassium iodide to solution of mercuric chloride, collecting, washing and drying the precipitate in the dark:

$$HgCl_2 + 2KI = 2KCl + HgI_2.$$

Properties. A red, amorphous, odorless, tasteless powder; insoluble in water, soluble in 130 parts alcohol, soluble in solution of potassium iodide or mercuric chloride. Turns yellow upon heating, melts and sublimes. Forms double salts with iodides.

Mercurous Oxide, Black or Sub-Oxide, Hg_2O. Made by action of caustic potash or soda on mercurous nitrate:

$$Hg_2(NO_3)_2 + 2KOH = 2KNO_3 + H_2O + Hg_2O.$$

Black, insoluble, odorless, tasteless powder.

Black Wash is made by triturating lime water with calomel, and contains calcium chloride and mercurous oxide; its formation is shown in the following equation:

$$Hg_2Cl_2 + Ca(OH)_2 = CaCl_2 + H_2O + Hg_2O.$$

Mercuric Oxide, HgO. Occurs in two forms; *yellow* and *red.*

Yellow Mercuric Oxide, yellow precipitate, is formed by adding solution of caustic soda to solution of mercuric chloride, washing and drying the precipitate:

$$HgCl_2 + 2NaOH = 2NaCl + H_2O + HgO.$$

A yellow, amorphous, insoluble powder.

Red Mercuric Oxide, red precipitate, is formed by heating the nitrate, or by triturating the nitrate with mercury and then heating:

$$Hg(NO_3)_2 = 2NO_2 + O + HgO.$$

$$Hg(NO_3)_2 + Hg = 2NO_2 + 2HgO.$$

It is a granular, crystalline, red, insoluble powder. Not so active as the yellow variety because not as finely subdivided.

Mercurous Sulphate, Hg_2SO_4. *Prepared* by heating strong sulphuric acid with an excess of mercury. Separates as a yellow, crystalline precipitate when sulphuric acid is added to solution of mercurous nitrate.

Properties. A yellow, crystalline solid.

Mercuric Sulphate, $HgSO_4$. *Made* by heating mercury with excess of sulphuric acid.

Occurs as a white, crystalline salt. When gently warmed becomes yellow, then red, and finally decomposes. When thrown into water it forms the basic salt.

Yellow Subsulphate of Mercury, *Turpeth mineral,* $Hg(HgO)_2SO_4$. Made by stirring powdered mercuric sulphate in a large volume of water.

Properties. "A heavy, lemon-yellow powder," odorless, tasteless and permanent in air. Slightly soluble in water; insoluble in alcohol. Used in medicine as alterative and emetic.

Mercurous Nitrate, $Hg_2(NO_3)_2$. *Made* by action of cold dilute nitric acid on mercury; the solution allowed to evaporate slowly, deposits crystals.

Properties. White or colorless crystals, soluble in water. Decomposed by much water into the basic salt. Used in solution as Millon's reagent.

Mercuric Nitrate, $Hg(NO_3)_2$. *Made* by dissolving red mercuric oxide in nitric acid, and may be obtained in deliquescent crystals. Used in medicine in "solution of mercury nitrate," which contains 60 per cent. of the salt, and has a specific gravity of 2.1. Also as "ointment of mercury nitrate" (citrine ointment), in which the solution is mixed with fat.

Mercuric Sulphide, HgS, is found in nature as cinnabar, a red mineral. Formed artificially as a black powder by action of hydrogen sulphide on solutions of mercury salts, and this

when sublimed forms the red variety. *Vermilion* is the finely-divided sulphide, made by subliming a mixture of sulphur and mercury.

Ammonia forms a number of double compounds with salts of mercury. When ammonia water is added to calomel a black compound is formed having the formula, NH_2Hg_2Cl, mercurous ammonium chloride.

By the action of ammonia water upon mercurous nitrate, a compound having the formula, $NH_2Hg_2NO_3$, is produced. It was called mercurius solubilis Hahnemanni.

A number of mercury-ammonium compounds are known, and in these compounds the mercury replaces the hydrogen of the ammonium radical.

Mercuric Ammonium Chloride, *White Precipitate,* NH_2HgCl, is *made* by pouring solution of mercuric chloride into ammonia water, when it forms as a white precipitate; this is washed and dried at 30°, with exclusion of light:

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

Properties. White, brittle, amorphous masses; odorless, earthy, metallic taste; insoluble in water or alcohol. Used in ointments in medicine.

Tests for Mercury Salts.

1. Hydrogen sulphide or ammonium sulphide: black precipitate.

2. Ammonium hydroxide: black precipitate with ous salts, white with ic salts.

3. Sodium or potassium carbonate: yellowish precipitate with ous salts; brownish-red with ic.

4. Potassium iodide: yellowish-green with ous salts; yellow, turning red and soluble in excess with ic salts.

5. Hydrochloric acid: white precipitate with ous salts; no change with ic.

6. Dry mercury compounds heated with sodium carbonate give metallic mercury, which forms globules on sides of test tube.

7. Bright metallic copper in solution of mercury salt with a drop of hydrochloric acid gives coating of mercury amalgam.

In poisoning by mercury salts there is salivation, soreness of the mouth and gums, abdominal pain, nausea, vomiting and diarrhœa. The antidote is egg albumen, which should be administered and then removed from the stomach, because the compound of albumen with mercury becomes soluble if it be allowed to remain.

CADMIUM.

Symbol, Cd. Atomic weight, 112. Quantivalence, II.

Cadmium is found in nature as the sulphide, usually associated with the ores of zinc. The metal may be obtained by heating the oxide with carbon.

Cadmium is a white metal, having a lustrous appearance and a fibrous structure. Its salts show great resemblance in properties to those of zinc, but the sulphide differs in having a yellow color and in not being soluble in dilute acids.

The compounds of cadmium are chiefly of scientific interest. The sulphate has been employed as an astringent in diseases of the eye: the sulphide is used as a yellow pigment.

Analytical Reactions.

Directions for analysis of an aqueous solution containing one or all of the metals, lead, copper, silver and mercury.

To the solution add hydrochloric acid, filter, and wash the precipitate with cold water.

<table>
<tr><td colspan="2">Precipitate.
Pb, Ag, Hg(ous)
Wash with boiling water.</td><td rowspan="2">Filtrate.
Pb, Cu, Hg(ic)
Divide into three portions.
Sol. 1. Add NH_4OH; blue color indicates copper.
Sol. 2. Add strip of metallic copper and heat; Hg deposits on the copper.
Sol. 3. Add H_2SO_4, evaporate nearly to dryness, and digest with small quantity of water; lead remains as a white insoluble powder.
(If the white precipitate form upon adding the acid no further reaction is required.)</td></tr>
<tr><td colspan="2">Ppt.
Ag, Hg(ous)
Add NH_4OH.</td><td>Filt.
Pb.
Add H_2SO_4; Ppt. White.</td></tr>
<tr><td>Ppt.
Hg.
Black.</td><td>Filt.
Ag.
Add HCl; Ppt. White.</td><td></td></tr>
</table>

METALS OF THE ARSENIC GROUP.

The elements *arsenic, antimony, tin, gold, platinum* and *molybdenum* are the members of the arsenic group of metals. They are precipitated from acid solution by hydrogen sulphide, and this precipitate, which is the sulphide of the metal, is insoluble in dilute acids, but soluble in ammonium sulphide or alkali hydroxide. In many cases they show a decided non-metallic character.

ARSENIC.

Symbol, As. Atomic Weight, 74. Valence, III and V.

Arsenic was known to the ancients in the form of its sulphides.

Occurrence in Nature. Sometimes in the free state in a crystalline form. Found in combination as oxide, As_2O_3, in *"arsenic bloom"*; as disulphide, As_2S_2, in *realgar,* and trisulphide, As_2S_3, in *orpiment.* The most abundant ore is the arsenio-sulphide of iron or *mispickel,* FeSAs. Sometimes found as arsenides of other metals, and in traces in some mineral waters.

Preparation. By heating the oxide with charcoal:

$$As_2O_3 + 3C = 3CO + As_2.$$

Properties. Arsenic is a steel-gray, metallic, crystalline solid; it is brittle, and can be easily powdered; its specific gravity is about 5.7. When heated to redness, without access of air, it volatilizes without fusing; in the presence of air it burns to the oxide. The metal is oxidized in part by exposure to moist air. Arsenic enters into direct combination with many other elements and, in its compounds, it is capable of taking the part of either a metal or non-metal.

Arsenic shows much resemblance to phosphorus and, like that element, forms several allotropic modifications. Amorphous arsenic forms when arsenic is heated in a tube through

which hydrogen is passing, or when arsine is heated as it passes through a glass tube; it deposits in the cool part of the tube as a black powder, having a specific gravity of 4.7.

Vapor density of arsenic is 150; molecular weight, 300; it therefore has four atoms in the molecule.

Hydrogen Arsenide, *Arsenetted Hydrogen, Arsine,* AsH_3. This compound is formed whenever arsenous or arsenic oxides or acids or their salts are brought in the presence of nascent hydrogen. In *properties* it is a colorless gas, having a disagreeable odor, and exceedingly poisonous when inhaled. It burns with a purple flame, forming arsenous oxide and water. If the tube through which the gas is passing be heated, amorphous metallic arsenic will be deposited just beyond the heated point, forming a black coloration. A piece of porcelain held in the flame of the burning gas acquires a deposit of metallic arsenic. By these means arsenic is easily recognized in Marsh's test. See page 228. Antimony salts give the same phenomena.

Arsenic Trichloride, $AsCl_3$. Can be made by passing chlorine over arsenous oxide. Usually prepared by heating arsenous oxide, sulphuric acid and sodium chloride in a retort, and collecting the distillate in a cooled receiver.

Properties. A colorless, oily liquid, having a tendency to form oxysalts when added to much water.

Arsenic Tri-iodide, *Iodide of Arsenic,* AsI_3. Can be *made* by direct union of the elements. More easily prepared by adding solution of potassium iodide to hot concentrated solution of arsenous oxide in hydrochloric acid, when it separates in crystals.

Properties. Red, crystalline masses, slight odor of iodine, slowly decomposed by exposure to light; soluble in water and alcohol. It is used in *Donovan's Solution, Solution of Iodide of Arsenic and Mercury,* in medicine, which contains one per cent. of the iodide of each of these metals.

Arsenic Tribromide is a colorless, crystalline solid, deliquescent and soluble.

Oxides and Acids of Arsenic.

Arsenic forms two oxides, which unite with water to form acids, showing the non-metallic character of the element: they are:

As_2O_3, **Arsenous Oxide**; and, As_2O_5, **Arsenic Oxide.**

Arsenous Oxide, *Arsenous Anhydride, White Arsenic, Ratsbane,* As_2O_3. Found in nature impure as *arseniolite* and as *arsenic bloom.*

Prepared by burning the metal. Also formed by roasting ores of metals containing arsenic, and obtained as a by-product. The impure oxide is purified by sublimation.

Properties. A white, slightly granular, crystalline powder, having a nauseous, metallic taste. When heated it sublimes without melting. It occurs in an amorphous form, as the product of distillation, in transparent, glassy masses, called *vitreous arsenic.* The amorphous variety gradually becomes opaque and crystalline. White arsenic is soluble in thirty to eighty parts water, the amorphous variety being the more soluble.

Used in medicine and the arts. Arsenous oxide is one of the most common poisons. This, and the other salts of arsenic, act as irritant poisons, producing burning pain in the throat, esophagus and abdomen; nausea, vomiting, purging and prostration. The antidote is *freshly precipitated* ferric hydroxide, which forms an insoluble compound with the poison.

Arsenous Acid, H_3AsO_3, forms when the arsenous oxide is dissolved in water:

$$As_2O_3 + 3H_2O = 2H_3AsO_3.$$

Its aqueous solution is colorless, and has an acid reaction. It has never been obtained in a pure state. It is tribasic and forms arsenites.

Liquor Acidi Arseniosi, Solution of Chloride of Arsenic of the U. S. P., is an aqueous solution of one per cent. arsenous oxide and five per cent. diluted hydrochloric acid.

Liquor Potassii Arsenitis, Fowler's Solution, is made by boiling one per cent. arsenous oxide with two per cent. potassium bicarbonate with water, and coloring the solution with three per cent. compound tincture of lavender.

Arsenic Oxide, *Arsenic Pentoxide,* As_2O_5. Made by heating arsenic acid until water is driven off, when the oxide is left as a white, glassy mass, soluble in water to form a solution of arsenic acid.

Arsenic Acid (*Ortho-arsenic Acid*), H_3AsO_4, is made by warming arsenous oxide with nitric acid, and evaporating to a syrupy consistency, when crystals of the acid separate.

Properties. A colorless, crystalline, soluble solid. By heating the acid to 180° water is driven off, and the pyro-acid is formed:

$$2H_3AsO_4 - H_2O = H_4As_2O_7.$$

By heating to 200°, two molecules of water are driven off and meta-arsenic acid forms:

$$2H_3AsO_4 - 2H_2O = H_2As_2O_6, \text{ or } 2HAsO_3.$$

These reactions show the great resemblance of arsenic to phosphorus.

Sodium Arsenate, Na_2HAsO_4. May be prepared by neutralizing arsenic acid with sodium carbonate:

$$H_3AsO_4 + Na_2CO_3 = Na_2HAsO_4 + H_2O + CO_2.$$

Usually prepared by fusing arsenous oxide, sodium carbonate and sodium nitrate together in a crucible, when the pyro-arsenate is formed, thus:

$$As_2O_3 + 2NaNO_3 + Na_2CO_3 = Na_4As_2O_7 + CO_2 + N_2O_3.$$

By dissolving the resulting mass in water and crystallizing, the salt is obtained:

$$Na_4As_2O_7 + 15H_2O = 2Na_2HAsO_4.7H_2O.$$

Properties. Colorless, transparent, prismatic crystals; freely soluble in water. Used in medicine in *liquor sodii arsenatis,* a one per cent. solution in water.

Sulphides of Arsenic. The elements arsenic and sulphur combine directly when heated together to form well-defined sulphides. The sulphides may also be formed by heating sulphur with arsenous oxide. Three of these are known—the *arsenic disulphide, arsenic trisulphide* and *arsenic pentasulphide.*

Arsenic Disulphide, As_2S_2, *Realgar,* is found in nature. It occurs in the form of red, glassy masses; insoluble in water; soluble in alkalies.

Arsenic Trisulphide, As_2S_3, *Orpiment,* is found in nature in yellow crystals. It forms when hydrogen sulphide is passed through an acidified solution of arsenic, as a yellow powder, insoluble in water, soluble in alkalies. With the alkalies it forms sulpharsenides, $K_2SAs_2S_3$.

Arsenic Pentasulphide, As_2S_5, is produced by fusing arsenic trisulphide with sulphur, and forms a yellow, fusible mass.

Tests for Arsenic.

1. Hydrogen sulphide in acidified solution of arsenic gives a yellow precipitate, soluble in ammonium sulphide or alkali hydroxide, reprecipitated by an acid.

2. Ammonio-nitrate of silver gives a yellow precipitate with solution of arsenous oxide; a chocolate brown with arsenic oxide; soluble in alkalies and acids.

3. *Bettendorf's Test.* Add to arsenic compound dissolved in hydrochloric acid, solution of stannous chloride in hydrochloric acid and tin foil and heat; a brown color forms.

4. *Gutzeit's Test.* Mix zinc, sulphuric acid and arsenic in a test-tube; fasten filter paper over mouth of tube and moisten with silver nitrate and dilute nitric acid; place in dark. Yellow stain forms; turns brown on moistening with water. Antimony gives brown stain.

5. Arsenic compounds heated with potassium carbonate and carbon liberate metallic arsenic.

6. Arsenic compounds heated on charcoal give odor of garlic.

7. *Reinsch's Test.* The arsenic solution is placed in a test-tube, a few drops of hydrochloric acid are added, and a strip of bright metallic copper is placed in the liquid. The tube is then heated carefully until the liquid boils, when a deposit of metallic arsenic appears on the surface of the copper. The strip of copper is removed, dried between folds of filter paper, and heated in the bottom of a dry clean test-tube. By this means the arsenic is volatilized from the copper, and combining with oxygen of the air, is deposited on a cool part of the tube in the form of crystals of arsenous oxide, which may be examined under the microscope.

8. *Fleitmann's Test.* A strong solution of caustic soda is placed in a small test-tube, a few fragments of zinc are added, and then the arsenic solution. A piece of filter paper, moistened with solution of silver nitrate, is now fastened over the open end of the test-tube. When the test-tube is heated, a black coloration appears on the filter paper. Antimony does not respond to this test. The chemical changes taking place in the above test are represented in the equation:

$$Zn + 2NaOH = Na_2ZnO_2 + H_2.$$

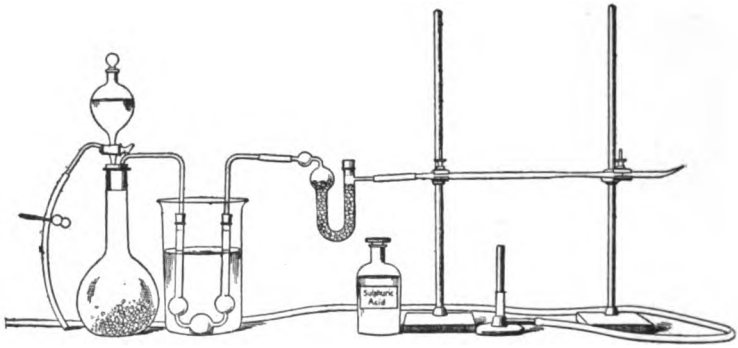
Nascent hydrogen combines with arsenic to form arsine, which in turn produces discoloration on the filter paper by liberating metallic silver.

9. *Marsh's Test.* The apparatus used in performing this test consists of a glass flask provided with a funnel tube and delivery tube. The delivery tube is connected with a wider tube filled with dried calcium chloride, and this connects with a hard glass tube drawn out to a fine calibre at intervals of two or three inches, and terminating in a contracted nozzle. Hy-

drogen is generated in the flask by using zinc and diluted sulphuric acid, and, when all air is expelled, the gas issuing from the extremity of the delivery tube is ignited and tested to see if the reagents contain arsenic as an impurity.

Having found that the hydrogen is pure, the arsenical liquid is added through the funnel tube. Upon heating the wider part of the delivery tube, a dark deposit of amorphous arsenic

FIG. 37.



Apparatus for Marsh's Test. (After Rockwood.)

makes its appearance just beyond the heated point at a constriction, and upon placing a cold porcelain surface in the flame a dark metallic spot of free arsenic appears.

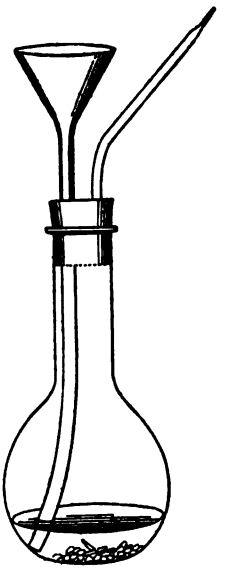
The character of the flame after adding arsenic is decidedly different from that produced by the burning hydrogen; it is larger, has a purple tint, gives off the odor of garlic, and is surmounted by a white cloud of arsenous oxide.

The reaction of Marsh's test is obtained from arsenic in the form of the oxides, their acids or salts, or the chloride; the sulphide is not suited for this test, and all organic matter must be absent when the test is applied.

The preparation of an organic substance containing arsenic for Marsh's test consists in heating the comminuted substance

with water, hydrochloric acid, and potassium chlorate to destroy the organic matter. The filtered liquid is then treated with hydrogen sulphide which precipitates the metals of the arsenic and lead groups, if they be present; the washed precipitate is treated with ammonium sulphide which dissolves out the arsenic and antimony; the resulting solution is evaporated to dryness and the dry residue is heated with sodium carbonate and sodium nitrate, thus forming sodium arsenate and antimonic oxide. By treating the resulting mass with warm water the arsenic is dissolved out and may be separated from antimonic oxide by filtration. The filtrate, containing the arsenic, can now be used for Marsh's test.

FIG. 38.



Student's Apparatus for Marsh's Test. (After Rockwood.)

Arsenic and antimony give the same reactions with Marsh's test, but the two spots may be distinguished by several tests, as follows:

The arsenic spot is soluble in solution of hypochlorites (calcium or sodium), the antimony spot is unaffected.

Dissolve the spot in nitric acid, evaporate to dryness, and add a drop of silver nitrate; a brick-red color forms with the arsenic spot, no color with the antimony spot.

Arsenic spot dissolves with ammonium sulphide and evaporated to dryness gives a yellow color; antimony spot treated in the same way gives orange-red.

ANTIMONY (Stibium).

Symbol, Sb. Atomic Weight, 119. Valence, III. and V.

Occurrence in Nature. Chiefly as the trisulphide, black antimony, or stibnite, Sb_2S_3; and with sulphur and metals in many ores. Antimony nearly always occurs in company with arsenic.

Preparation. By roasting in air and heating the resulting oxide with carbon.

Properties. A brittle, bluish-white, crystalline metal; fuses at 450°, and volatilizes at a higher temperature when air is excluded; burns when heated in air, forming the oxide; combines directly with the halogens; inflames in chlorine gas.

Hydrogen Antimonide, *Stibine,* SbH_3. *Formed* by a process analogous to that of hydrogen arsenide.

Properties. Colorless gas, burns with formation of antimonic oxide.

Antimonous Chloride, *Trichloride of Antimony,* $SbCl_3$.

Preparation. By heating the trisulphide with hydrochloric acid, evaporating to dryness and distilling:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2.$$

Properties. A white, crystalline, semi-transparent, soft mass, known as butter of antimony, fusing at 73° and boiling at 223°. The salt is deliquescent; it dissolves in water acidified with HCl. The solution poured in much water becomes turbid from precipitation of the oxychloride, or *powder of Algaroth:*

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

Antimony Pentachloride, *Antimonic Chloride,* $SbCl_5$. Formed by the action of an excess of chlorine on the trichloride. It is a yellowish liquid, and fumes in the air.

The *tribromide* and *tri-iodide* are known.

Oxygen Compounds of Antimony. Antimony forms two oxides: *Antimonous Oxide,* Sb_2O_3, and *Antimonic Oxide,*

Sb_2O_5. These resemble the corresponding compounds of arsenic. The first has basic properties; the second, by union with water, forms antimonic acid, pyroantimonic acid and metantimonic acid, like phosphorus.

Antimonous Oxide, Antimony Trioxide, Sb_2O_3.

Preparation. By burning the metal in air. By adding sodium carbonate to the solution of the trichloride and heating to boiling:

$$2SbCl_3 + 3Na_2CO_3 + H_2O = 2HSbO_2 + 6NaCl + 3CO_2.$$

$$2HSbO_2 + \text{heat} = Sb_2O_3 + H_2O.$$

Properties. A heavy, grayish-white powder, soluble in hydrochloric acid. This salt dissolves in solution of potassium bitartrate, forming *tartar emetic.*

Antimonic Oxide, or *Pentoxide of Antimony,* Sb_2O_5. *Preparation.* By action of strong nitric acid on metallic antimony, evaporating to dryness, and gently heating the residue.

Properties. A pale, straw-colored powder.

Antimonous Acid, *Ortho-antimonous Acid,* H_3SbO_3, precipitates when sulphuric acid is added to tartar emetic solution. A white powder.

Metantimonous Acid, $HSbO_2$, forms when $SbCl_3$ is decomposed with sodium carbonate. A white, amorphous, insoluble powder.

Antimonic Acid, *Ortho-antimonic Acid,* H_3SbO_4. This acid is formed when antimony pentachloride is dropped into water. It separates from solution as a gelatinous precipitate, of acid reaction, and astringent taste. When heated to 100° it loses water and forms *pyro-antimonic acid,* $H_4Sb_2O_7$.

The sodium salt of pyro-antimonic acid, $Na_2H_2Sb_2O_7.6H_2O$, is remarkable in being the only insoluble compound of sodium.

Metantimonic Acid, $HSbO_3$, forms when pyro-antimonic acid is heated to about 200°, or when powdered antimony is heated with nitric acid. It is a white insoluble powder, and a weak monobasic acid.

Compounds of Antimony with Sulphur.

Antimony Trisulphide, *Antimonous Sulphide, Antimony Sulphide,* Sb_2S_3. *Occurs in nature* with impurities, and sepa-

rated by heating when the sulphide melts and is allowed to flow into suitable vessels.

Properties. Steel-gray, metallic lustre, or dark, grayish powder, insoluble in water, volatilized by high heat. The purified antimony prepared by washing the above with ammonia water. By passing H_2S through an acidified solution of antimony, the trisulphide is obtained as an orange-red powder which, when heated, is converted into the black variety.

Sulphurated Antimony, Kermes Mineral, is an oxysulphide of antimony, $Sb_2S_3Sb_2O_3$, and is formed by boiling antimonous sulphide with solution of sodium hydroxide and adding sulphuric acid. The precipitate formed is washed and dried.

Properties. A reddish-brown, amorphous powder; insoluble in water, soluble in hydrochloric acid, or sodium hydroxide.

Antimony Pentasulphide, *Golden Sulphuret of Antimony,* Sb_2S_5. *Prepared* by the action of H_2S on acid solution of antimonic acid.

Properties. An orange-red powder which, when heated, decomposes to Sb_2S_3 and S_2.

Tests for Antimony.

1. With hydrogen sulphide in acid solution compounds of antimony give an orange-red precipitate, soluble in ammonium sulphide. This precipitate is soluble in *strong* hydrochloric acid—differing from arsenic.

2. Solutions heated with metallic copper give a black deposit of antimony which, when heated in dry test-tube, gives a deposit of antimonous oxide on the glass.

3. Gutzeit's test gives a brown spot without the antecedent yellow seen with arsenic.

4. Marsh's test gives antimony spot distinguished from arsenic spot as described in the tests for arsenic.

TIN (Stannum).

Symbol, Sn. Atomic Weight, 118. Valence, II. and IV.

Occurrence in Nature. As the oxide, SnO_2, in "tin stone." Sometimes found as sulphide, usually with other metals.

Preparation. By heating the oxide with carbon.

Properties. A white, malleable metal, lustrous appearance, crystalline. Fuses at 233°; combines directly with most of the non-metals; forms two classes of salts, stannous and stannic; bivalent in stannous salts and quadrivalent in stannic.

Stannous Chloride, $SnCl_2$ (Protochloride).

$$Sn + 2HCl = SnCl_2 + H_2.$$

The anhydrous form may be obtained, by heating tin in hydrochloric acid gas, as a gray, fatty-looking mass. Usually prepared by dissolving tin in hydrochloric acid, boiling down and allowing to crystallize.

Properties. Colorless, prismatic needles; forms oxychloride with much water; strong reducing agent—precipitates arsenic, mercury, gold, in metallic state.

Stannic Chloride, *Perchloride of Tin,* $SnCl_4$. May be made from stannous chloride by passing chlorine through its solution, or by dissolving the metal in nitric and hydrochloric acid with aid of heat.

Properties. A colorless, fuming liquid, combines with 4 molecules water to form a crystalline compound.

Test for Tin Salts.

1. Hydrogen sulphide precipitates stannous salts, brown; stannic salts, yellow.

GOLD (Aurum).

Symbol, Au. Atomic Weight, 196.7. Valence, I. and III.

Known from the earliest times.

Occurrence in Nature. Very widely distributed in nature, but usually in very small quantities. Usually found in free

state in granules, often in company with silver, copper, iron, or platinum. Sometimes found, though rarely, amalgamated with mercury.

Preparation. Gold is prepared by washing the sand or crushed ores in which it occurs, in such a way that the lighter material of the ores is carried away, and gold remains in the heavy deposit. This deposit is mixed with mercury which dissolves out the gold, forming an amalgam, and the amalgam is then heated, driving off the mercury and leaving the gold.

Properties. Gold is an orange-yellow metal; it is soft, malleable, ductile and capable of taking a high polish; its specific gravity is 19.36; its fusing point is 1200°.

The use of gold in making articles of jewelry and coins is supplemented by the addition of copper or silver to give hardness to the metal. The fineness of jewelry is expressed in carats, or twenty-fourths: eighteen carats fineness is eighteen parts of pure gold in twenty-four of the alloy, or 18/24 gold and 6/24 base metal; fourteen carats is 14/24 gold, and 10/24 base metal, etc.

Refined gold is gold from which such metals as copper or silver have been removed by treatment with sulphuric or nitric acids.

Gold foil is made by beating gold into exceedingly thin sheets; its malleability being so great as to permit a thinness of 1/256,000 of an inch.

Cohesive gold, used in dentistry, is made by heating gold foil to redness: it differs from ordinary gold in having a spongy appearance.

Gold is not affected by any of the strong mineral acids except selenic acid; it is dissolved by nitro-hydrochloric acid, forming the chloride; it is attacked by chlorine, bromine, or mercury. Gold is univalent in aurous compounds; it is trivalent in auric compounds, the latter are the only salts of interest.

Gold Chloride, $AuCl_3$, made by dissolving gold in nitrohydrochloric acid and crystallizing from the solution, is a granular, yellow, soluble powder. When this salt is mixed with solution of sodium chloride, and the mixed solutions are evaporated, it forms the chloride of gold and sodium, a yellow, granular, soluble solid, used in medicine.

Tests for Gold.

1. H_2S gives brown Au_2S_3, soluble in ammonium sulphide.
2. To a solution of gold salt add solution of ferrous sulphate and allow to stand; metallic gold is precipitated in a fine state of subdivision.
3. Solution of sulphurous acid precipitates metallic gold from solution.

PLATINUM.

Symbol, Pt. Atomic Weight, 193. Valence, II. and IV.

Occurrence in Nature. Widely distributed in small quantity. Occurs free with iridium, osmium, ruthenium and gold in grains in sand of rivers, usually. Found in Ural mountains.

Prepared by treating ores with nitric acid, then hydrochloric acid to remove impurities, and the residue is dissolved with hot nitrohydrochloric. The solution of platinum thus obtained is precipitated by ammonium chloride, and the precipitate heated, leaving *spongy platinum,* which is fused and welded to solid mass. Another method consists in heating with lead and lead sulphide, then oxidizing the lead, which leaves the platinum. Platinum is melted in a furnace of lime by the oxyhydrogen flame.

Properties. Platinum is a grayish-white metal, rather soft and not oxidizable; it is ductile, malleable and infusible by ordinary heat; its specific gravity is 21.15.

This metal is not soluble in acids except nitrohydrochloric; it is attacked by fused alkaline hydroxides, nitrates, sulphides

and cyanides; it has the power to absorb oxygen, but is not attacked by this element.

Platinum black is metallic platinum in a state of fine subdivision, obtained from a solution of the chloride as a precipitate by the action of strong reducing agents: it can be made by adding to a solution of the chloride, an alkaline carbonate and sugar, and boiling.

Platinum Perchloride, $PtCl_4.5H_2O$. When platinum is dissolved in nitro-hydrochloric acid and the solution evaporated with hydrochloric acid to expel nitric acid, there results chloroplatinic acid, $PtCl_4 2HCl.6H_2O$. By decomposing one molecule of this salt with two molecules of silver nitrate, filtering the precipitate, the filtrate gives crystals of platinum chloride, $PtCl_4.5H_2O$.

Platinum perchloride is a heavy, brown, deliquescent, soluble salt, whose solution has a beautiful golden-yellow color. This salt is largely used as a reagent for precipitating the salts of potassium.

Tests for Platinum.

1. To solution of platinum salt add excess of sodium carbonate and some cane sugar and boil; the platinum is precipitated as a fine black powder in the metallic state.

2. Add solution of ammonium chloride; a golden-yellow, granular precipitate forms, consisting of the double chloride of platinum and ammonium.

MOLYBDENUM.

Symbol, Mo. Atomic Weight, 95.

Molybdenum is found in nature as the sulphide: it is prepared by heating the chloride or oxide in a stream of hydrogen.

In properties molybdenum is a silvery-white, hard, and more infusible metal than platinum; its specific gravity is 8.6.

Molybdenum Oxide, MoO_3, is formed by roasting the sulphide; it combines with water to form molybdic acid, which unites with alkalies to form molybdates. Ammonium molybdate, dissolved in nitric acid, is used as a reagent for phosphoric acid, with which it gives a yellow precipitate.

Directions for Analysis of an Aqueous Solution of One or All of the Important Metals, As, Sb, Pb, Cu, Ag, Hg, Fe, Zn, Al, Ca, Sr, Ba, K, Na, NH_4. Add Excess of HCl; Filter.

Precipitate
Pb, Ag, Hg(ous).
Wash with cold water, transfer to test-tube, boil with water, filter.

- **Ppt.** Ag, Hg(ous). Wash, add NH_4OH, filter.
  - **Ppt.** Hg(ous); Black.
  - **Filtrate,** Ag. Add HNO_3; White ppt.
- **Filtrate,** Pb. Divide into 2 portions
  - To 1 add K_2CrO_4; ppt. yellow.
  - To 2 add H_2SO_4, ppt. white.

Filtrate.
Cu, Hg(ic), As, Sb, Pb, Fe, Al, Zn, Ba, Ca, Sr, Mg, K, Na, NH_4.
Pass H_2S through the liquid as long as a precipitate forms; filter.

Precipitate.
Cu, Pb, Hg(ic), As, Sb.
Wash; transfer to test-tube and digest with $(NH_4)_2S$; filter.

- **Ppt.** Pb, Cu, Hg(ic) Digest with dil. HNO_3 (1 to 2); filter.
  - **Ppt.** Hg. Wash; dissolve in aqua regia, warm to drive off excess of acid, dilute with water, and test for Hg with copper foil.
  - **Filtrate.** Pb, Cu, Add H_2SO_4; filter.
    - **Ppt.** Pb; white.
    - **Filtrate.** Cu, Add NH_4OH; blue color.
- **Filtrate.** As, Sb. Add, $HC_2H_3O_2$, boil, digest ppt. with HCl, dilute, filter.
  - **Ppt.** As; yellow.
  - **Filt.** Sb. Add H_2S; orange ppt.

Filtrate.
Fe, Al, Zn, Ba, Ca, Sr, Mg, K, Na, NH_4.
Add NH_4OH, $(NH_4)_2S$, and filter.

- **Ppt.** Fe, Al, Zn. Wash, dissolve in HCl, add KOH, agitate, filter.
  - **Ppt.** Fe. Test orig. solution to determine whether ous or ic.
  - **Filt.** Al, Zn. Neutralize with HCl, add NH_4OH, filter.
    - **Ppt.** Al, white.
    - **Filt.** Zn. Add $(NH_4)_2S$, ppt. white.
- **Filt.** Ba, Ca, Sr, Mg, K, Na, NH_4. Add $(NH_4)_2CO_3$, boil, filter.
  - **Ppt.** Ba, Ca, Sr. Wash, dissolve in $HC_2H_3O_2$, boil, add $K_2Cr_2O_7$.
    - **Ppt.** Ba. yellow.
    - **Filt.** Ca, Sr. Add K_2CrO_4.
      - **Ppt.** Sr, yellow.
      - **Filt.** Ca. Add $(NH_4)_2C_2O_4$, ppt. white.
  - **Filt.** Mg, K, Na, NH_4. Add $(NH_4)_2HPO_4$ filter.
    - **Ppt.** Mg, white.
    - **Filt.** K, Na, NH_4, evap. to dryness, heat, dissolve in H_2O, and add $PtCl_4$.
      - **Ppt.** K, yellow.
      - **Filt.** Na, Apply flame test for Na. Test orig. sol. for NH_4 with NaOH.

PART IV.

ORGANIC CHEMISTRY.

GENERAL CONSIDERATIONS.

The study of the *compounds of carbon* constitutes a special branch of chemical science. Mainly on account of the great number, and partly on account of peculiarities in chemical conduct, it is customary to consider these compounds by themselves. The subdivision of General Chemistry into inorganic and organic by the older chemists was intended to include bodies of mineral origin in the former class, and bodies obtained from plants and animals in the latter. The supposed radical difference in the nature of bodies in the two classes was due to a belief that organic substances were formed under the mysterious influence of " vital force."

For a long time it was impossible to form organic bodies from the elements, either directly or indirectly, and their peculiar properties and the complexity of the changes which they undergo could not be interpreted in the laws then known. Organic and inorganic bodies were therefore regarded in the light of substances having essential differences in character. Finally, in 1828, Wohler succeeded in preparing urea by artificial means. Soon afterwards, many other compounds, which hitherto had been obtained only as the product of living tissues, were prepared in the laboratory. These, and other experiments, led to the conclusion that the laws of chemistry apply alike to inorganic and organic substances, all being included in one great science.

The old interpretation of the theory of "vital force" has been abandoned, and we know that compounds formed in living tissues are not different from the same compounds produced artificially. On the other hand, it seems to have been clearly shown in recent investigations, that chemical changes occur under the influence of cellular activity, which would not occur under ordinary conditions.

Organic chemistry, according to the present views, is the chemistry of the compounds of carbon. In accepting this definition we must leave out of consideration carbonic acid and the carbonates of the metals, but this objection to the term is not sufficient for its abandonment. The term, "hydrocarbon compounds," has been suggested as an appropriate definition.

The distinction between organic bodies and organized bodies should be clearly drawn at the outset. An organic body is a definite chemical compound, such as alcohol, chloroform, chloral; an organized body is made up of many different compounds, it has a characteristic cellular structure, and usually enters into the formation of some organ of a plant or animal.

The Elements forming organic compounds are very few, when we take into consideration the great number of these compounds. The elements carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus and iron are the ones usually present. Many hundreds of organic bodies are known which contain only carbon and hydrogen, or carbon, hydrogen and oxygen. Other elements are sometimes found in organic bodies, and it is possible to introduce any element into an organic form of combination by artificial means.

The formation of such a great number of compounds from so few elements is explained in the fact that the elements concerned exhibit extreme differences in physical and chemical properties. A further explanation is found in the linking power which the atoms of some of these elements possess; a

property which enables an atom to partly satisfy the affinities of its fellow, leaving other affinities to be satisfied by the atoms of other elements.

Source of Organic Compounds. Most organic bodies are formed by artificial means in the chemical laboratory, but they are generally prepared from others which occur ready-formed in nature. *Crude Petroleum* is used for the preparation of a great many of these compounds, especially those of the hydrocarbon series, and many are prepared from *coal-tar, wood-tar* and *bone-oil.* Many organic bodies are prepared from others by *fermentation* and *destructive distillation.*

The Separation and Purification of organic bodies is accomplished by taking advantage of differences in physical and chemical properties. The slightly soluble ones in solution may be made to crystallize out, leaving behind the more soluble ones, and the "mother liquor" resulting therefrom may be made to yield a second crop of crystals, or even a third. This is known as *fractional crystallization.*

Advantage is taken of differences in boiling point, and they are separated by *fractional distillation.* Those of low melting point may be heated to the temperature of fusion and allowed to run off from others of higher melting point. Separation by making use of chemical properties is accomplished by causing a substance to unite with the compound to be removed, or to cause its liberation from combination with other bodies, etc. *Proximate analysis* is a term frequently used to indicate the separation of organic bodies from each other, as above described.

Analysis of Organic Compounds. The qualitative analysis of an organic compound is of little value except to establish the organic nature of the substance. The knowledge that a given substance contains carbon and hydrogen, or carbon, hydrogen and oxygen, would not indicate what the substance

is, because many hundreds of compounds contain the elements named. On the other hand, in the study of inorganic bodies, to find that a compound is composed of iodine and mercury would indicate either mercurous or mercuric iodide, because these are the only compounds containing these two elements, and a few simple tests would serve to distinguish between the two.

The quantitative analysis for determining the elements of an organic body is frequently spoken of as an "*elementary, or ultimate analysis.*"

1. *Qualitative Analysis.* The presence of *carbon* is easily shown in many cases by charring of the substance when heated on platinum foil. In other cases, when the above test cannot be applied, the substance is heated in a glass tube with copper oxide which converts carbon into carbon dioxide, and this compound may be recognized by passing it into lime water.

Hydrogen may be determined by heating the substance with copper oxide when it is converted by oxidation into water. This will condense in a cool part of the tube.

Nitrogen is determined by heating with dry soda-lime (a mixture of one part of sodium hydroxide and two parts of calcium hydroxide) when it comes off as ammonia and can be recognized by appropriate tests.

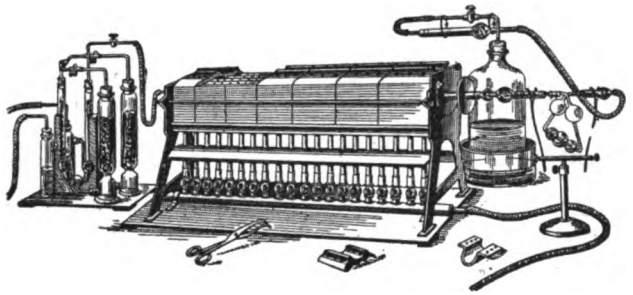
Phosphorus and *sulphur* are recognized by heating the substance with sodium nitrate and carbonate, in a crucible, to form sodium phosphate and sulphate. The mass is washed with water and the solution tested for these salts.

Oxygen is not usually determined by qualitative methods.

2. *Quantitative Analysis.* The hydrogen and carbon are determined by heating the dry substance with copper oxide in a combustion tube and collecting and weighing the escaping vapors of water and carbon dioxide. The water vapor is collected in a previously weighed U-shaped tube of dried calcium

chloride; increase in weight represents the weight of water formed, and from this the weight of hydrogen is easily calculated. The carbon dioxide is collected and weighed, in like manner, in bulbs containing potassium hydroxide solution, and from the weight of carbon dioxide obtained the weight of carbon is calculated.

FIG. 39.



Combustion Furnace. (After Bartley.)

The quantity of nitrogen is determined by heating the organic substance with soda-lime and passing the ammonia thus formed into hydrochloric acid. The resulting solution is evaporated on a water bath, the dry residue of ammonium chloride is weighed and from this is calculated the weight of nitrogen.

Oxygen is determined by difference, after accounting for all other elements present.

Phosphorus and *sulphur* are converted into phosphoric and sulphuric acids as above described, and the quantity of each is calculated from the weights of these salts.

The results of the analysis are usually first expressed in a percentage formula.

For example:

Analysis of 44 gms. dried organic substance gives:	
88 gms. CO_2, representing	24 gms. Carbon,
36 gms. H_2O, representing	4 gms. Hydrogen,
and a remainder of	16 gms. Oxygen,
other elements being absent.	—
	44 gms. substance.

Percentage formula:

$$\text{Carbon} = \frac{24 \times 100}{44} = 55+ \text{ per cent.}$$

$$\text{Hydrogen} = \frac{4 \times 100}{44} = 9+ \text{ per cent.}$$

$$\text{Oxygen} = \frac{16 \times 100}{44} = 36+ \text{ per cent.}$$

$$100$$

The Empirical Formula is the simplest expression of the *relative* numbers of atoms in the molecule, without giving the actual numbers. It may be determined from the percentage formula by dividing the percentage of each element by its atomic weight, and dividing the quotients by the greatest common divisor, so as to express these relations in their simplest terms.

For example:

Carbon,	54.48 per cent., ÷ 12 = 4.54	÷ 2.27 =	Carbon, 2
Hydrogen,	9.21 per cent., ÷ 1 = 9.21		Hydrogen, 4.06
Oxygen,	36.31 per cent., ÷ 16 = 2.27		Oxygen, 1
	100.00		

Or, approximately, C_2H_4O, the empirical formula.

The Molecular Formula expresses what is included in the empirical formula and, in addition to this, it expresses the actual number of atoms in the molecule. The molecular formula is most readily determined from the empirical by taking the vapor density of the substance as compared with hydrogen, and referring to the law of Avogadro.

For example:

If, in the above compound, C_2H_4O represents its true molecular formula, the vapor density, when compared with hydrogen, would be 22. If its vapor density is found to be 44, its molecular formula would be $C_4H_8O_2$. (See methods for determining molecular weight, page 73.)

It is not always possible to vaporize the substance whose molecular formula is to be determined and, in these cases, it is necessary to study the chemical reactions and decompositions.

Structural, Constitutional, or Graphic Formulas. These formulas represent all that is shown in the empirical and molecular formula and, in addition, they represent the relative arrangement of the atoms in the molecule, the chemical changes the compound is likely to undergo, and its relations to other compounds. It must be remembered that they are not intended to show the actual position in space of the atoms.

In order to get a clear idea as to the exact significance of a graphic formula, it is well to study how such a formula is determined, thus:

When the molecular formula has been determined, the next thing to be done is to study the compound by physical and chemical methods, in order to ascertain just how it behaves under all the conditions that can be applied. In this way many facts are discovered in reference to the substance—in other words, we have acquainted ourselves with many of its properties. The next step is to embody these facts in a formula which will give them expression. How this is done can be shown best by an example. In the case of acetic acid, the molecular formula is found to be $C_2H_4O_2$. It may be shown that one-fourth of the hydrogen can be replaced by a metal ($C_2H_3KO_2$), and thus it is seen that one of the hydrogen atoms is different from the others, since they cannot be replaced. This fact is expressed by writing the formula for acetic acid, $H.C_2H_3O_2$.

Again, by treating acetic acid with phosphorus trichloride, a compound having the formula C_2H_3OCl is formed, and the acid loses one atom of hydrogen and one of oxygen. If this chlorine compound be treated with water, acetic acid is regenerated by entrance of the atom of hydrogen and of oxygen:

$$C_2H_3OCl + H_2O = HCl + C_2H_4O_2.$$

This reaction shows that an atom of hydrogen and an atom of oxygen are closely associated in the molecule, since they leave and re-enter it together. This fact is expressed by the formula:

$$C_2H_3O.OH.$$

The chlorine compound formed in the above experiment contains no hydrogen that can be replaced by metals, and thus we know that the replaceable hydrogen of acetic acid, expressed in the formula, $H.C_2H_3O_2$, is closely associated with oxygen, and is the same as that represented in the formula, $C_2H_3O.OH$.

By experiments of like nature it can be shown that the other oxygen atom is closely associated with a carbon atom, and this fact, with the others determined, is expressed by the formula, $CH_3.CO.OH$. These facts are determined by analysis and may be confirmed by synthesis.

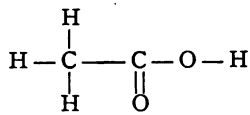
The synthesis of acetic acid may be accomplished by causing marsh gas, CH_4, to act upon carbonyl chloride, $COCl_2$, thus:

$$CH_4 + COCl_2 = C_2H_3OCl + HCl.$$

The compound, C_2H_3OCl, is found to be identical with the one formed by the action of phosphorus trichloride on acetic acid, and the correctness of the formula, $CH_3.CO.OH$, is strongly indicated.

These formulæ are thus seen to express not only the composition of substances but, to a great extent, properties as well.

When we call to our aid the valency hypothesis, and give expression in our formula of the quantivalence of each atom, we have a completed graphic formula for acetic acid, thus:



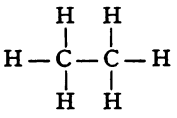
The graphic formula when viewed in this light is a valuable aid to the study of chemistry, but too much importance should

not be attached to the formula itself to the exclusion of that which it represents.

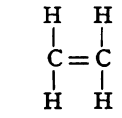
Linking Power of Atoms. The power possessed by some atoms of partly satisfying the chemical affinities of other atoms of the same or different elements, leaving affinities to be satisfied by other atoms, is known as linking, or chain formation. This power is very highly developed in the atoms of carbon and oxygen, and is well shown in the types of graphic formulæ.

Types of graphic formulæ showing linking power of carbon atoms:

1. *By varying number of valence units—*



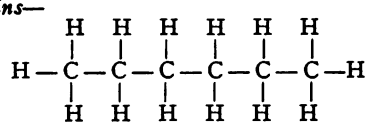
Ethane



Ethene, or ethylene

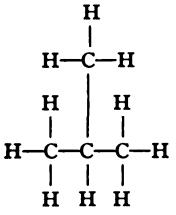
Ethine, or acetylene

2. *Simple Chains—*



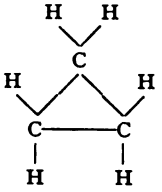
Hexane

3. *Simple chain with lateral attachment—*

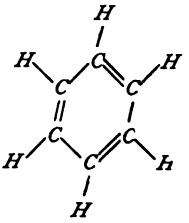


Trimethyl-methane

4. *Simple closed chains—*

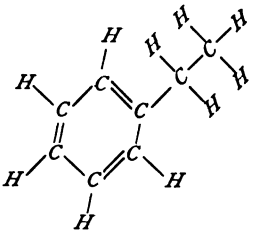


Trimethylene



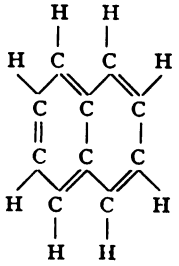
Benzene

5. *Closed chains with lateral attachments—*



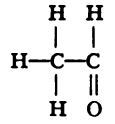
Ethyl-benzene

6. *Multiple closed chains—*

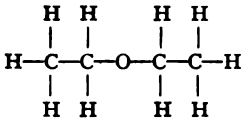


Naphthalene

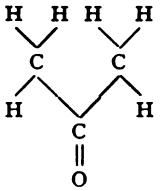
7. Linking of oxygen atoms—



Ethyl-aldehyde



Ethyl-ether



Acetone

A Radical is an unsaturated group of atoms behaving, in many respects, like a single atom. It is capable of passing as a unit from one compound to another in chemical changes. A radical may be obtained by removal of one or more atoms from a saturated compound but it is not necessary for it to exist alone; in fact, radicals are usually incapable of separate existence. The radical of water is hydroxyl, OH, obtained by removal of an atom of hydrogen. From marsh gas, CH_4, four radicals may be obtained by removal of one, two, three or four atoms of hydrogen.

Substitution is a chemical change by which an atom, or group of atoms, is replaced by another atom, or group of atoms. It is a very common form of chemical change in organic bodies, and is plainly shown in the following equation which represents the replacement of hydrogen in benzene, C_6H_6, by the radical NO_2, of nitric acid:

$$C_6H_6 + HONO_2 = C_6H_5NO_2 + H_2O.$$

A Derivative is a compound formed from some other by a chemical change. Alcohols are derivatives of hydrocarbons, formed from them by replacement of hydrogen by the radical hydroxyl, thus:

C_2H_6.	C_2H_5OH.
Hydrocarbon	Alcohol derivative

An Homologous Series of organic compounds is one in which each of the members differs from the next of the series

by the term CH_2. An homologous series of organic compounds is represented thus:

$$CH_4,\ C_2H_6,\ C_3H_8,\ C_4H_{10},\ C_5H_{12},\ C_6H_{14},\ \&c.$$

An Isologous Series is one in which each member differs from the next of the series by the term H_2. An isologous series is represented thus:

$$C_3H_2,\ C_4H_4,\ C_5H_6,\ C_6H_8,\ \&c.$$

Isomerism. Bodies composed of the same elements in the same proportions by weight are found, in some cases, to possess different properties; these are said to be isomeric with each other. Isomeric bodies may be either polymeric or metameric.

Polymeric bodies are those having the same proportionate number of atoms of the same elements in the molecule. These formulas represent polymeric bodies:

$$C_2H_2,\ C_4H_4,\ C_6H_6,\ \&c.$$

Metameric bodies are those having the same actual numbers of atoms of the same elements in the molecule, the difference in properties here depending upon a difference in the arrangement of the atoms. Ethyl acetate and butyric acid both have the empirical formula $C_4H_8O_2$, but the arrangement of atoms in ethyl acetate is represented by the formula, $C_2H_5.C_2H_3O_2$; the arrangement in butyric acid by the formula, $H.C_4H_7O_2$.

Stereoisomerism is a form of isomerism dependent upon differences in the space relations of the atoms in the molecules of two or more compounds, otherwise the same. Two bodies are said to be stereoisomeric when they show differences in the geometrical arrangement of atoms in the molecule and act differently upon the ray of polarized light.

The study of stereoisomerism is conducted by making observations of the action of bodies upon the ray of polarized light.

General Properties of Organic Bodies. The properties are dependent to a great extent upon the properties of the constituent elements. Organic bodies are found as solids,

liquids and gases. They are gaseous when the molecule is light, and contains a small amount of carbon as compared to the hydrogen or oxygen. With increase in the proportion of carbon, increase in molecular weight, and increase in specific gravity, there is augmentation in the density of the compound —passing from a tenuous to a dense gas, from a gas to a liquid, and from a liquid to a solid. In this way, compounds containing little carbon of small molecular weight are gases; those containing much carbon of great molecular weight are solids.

Organic bodies show every variety of color, odor and taste. Some serve for food, while others are violently poisonous. They are combustible, because of this property in carbon and hydrogen. They occur as acids, bases and salts. Some are active and some are very inert. In short, they present every variety of properties; and it is surprising that so few elements are capable of forming such a great number of compounds showing such dissimilarity.

Chemical Change in Organic Bodies is promoted by those conditions which favor chemical action in general, but the character of the reaction is frequently different from that which we have seen heretofore. Some of the more important chemical changes which have been observed to occur in organic bodies are given, as follows:

1. A rearrangement of the atoms in the molecule, whereby the molecular structure of the substance is changed, resulting in a corresponding change in properties. This kind of change often occurs spontaneously, and is seen in the slow conversion of oil of lemon into oil of turpentine by the lapse of time.

2. Splitting of a molecule into two or more compounds of simpler nature. This kind of change can be seen in the formation of ethyl alcohol and carbon dioxide from glucose during the process of fermentation, thus:

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

3. The union of two or more molecules of the same or of different kinds, thus:

$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$

4. The removal of atoms from a molecule, with or without replacement by other atoms, thus:

$$\underset{\text{Alcohol}}{C_2H_6O} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Aldehyde}}{C_2H_4O} + \underset{\text{Hydrochloric acid}}{2HCl.}$$

$$\underset{\text{Aldehyde}}{C_2H_4O} + \underset{\text{Chlorine}}{3Cl_2} = \underset{\text{Chloral}}{C_2HCl_3O} + \underset{\text{Hydrochloric acid}}{3HCl.}$$

Action of Heat Upon Organic Bodies. Some organic bodies are volatilized by the action of heat but on account of the instability of the molecule many of them are decomposed. Heating an organic body in a closed vessel, so as to exclude air and form volatile products, is known as *destructive distillation.* The nature of the products formed by destructive distillation depend upon the nature of the substance heated and also upon the degree of heat employed. The products thus formed have a smaller number of atoms in the molecule, and are less complex in structure than the original substance. Destructive distillation furnishes the means of obtaining a great many useful organic compounds, such as wood alcohol, creosote, carbolic acid, acetic acid, naphthaline, etc.

Action of Oxygen. On account of the presence of hydrogen and carbon all organic bodies are capable of oxidation. Oxidation occurring with sufficient degree of intensity to furnish heat and light is called *combustion.* Oxidation may proceed slowly throughout a long period of time without light or sensible heat; it is then called decay or slow combustion. It is worthy of note, that of all organic bodies found in nature none contains a sufficient amount of oxygen to oxidize all of the carbon and hydrogen found in the molecule; such bodies may be made by artificial means, however, and they constitute highly explosive compounds.

Products formed by rapid oxidation of organic bodies are carbonic acid, water, phosphoric and sulphuric acids, from the elements carbon, hydrogen, phosphorus and sulphur, respectively, when present.

The *ultimate products* are the same in rapid and slow combustion, but when organic bodies undergo slow oxidation many intermediate substances are formed before the state of complete oxidation is reached. This is shown in the following equations which represent the changes occurring in rapid and slow oxidation of alcohol.

Rapid oxidation of alcohol:

$$\underset{\text{Alcohol}}{C_2H_6O} + \underset{\text{Oxygen}}{3O_2} = \underset{\text{Carbon dioxide}}{2CO_2} + \underset{\text{Water}}{3H_2O}.$$

Slow oxidation of alcohol:

$$\underset{\text{Alcohol}}{C_2H_6O} + \underset{\text{Oxygen}}{O} = \underset{\text{Aldehyde}}{C_2H_4O} + \underset{\text{Water}}{H_2O}.$$

$$\underset{\text{Aldehyde}}{C_2H_4O} + \underset{\text{Oxygen}}{O} = \underset{\text{Acetic acid}}{C_2H_4O_2}.$$

Oxidation is facilitated by the presence of warmth and moisture, and it is indefinitely retarded by keeping the substance perfectly dry.

Fermentation and Putrefaction consist of chemical changes in which the molecule of the organic body is split up into two or more molecules of simpler composition. For these changes to take place three factors are necessary—*moisture, favorable temperature, and the presence of a ferment.*

The temperatures favoring fermentation and putrefaction range between 25° and 40° C., or 77° and 104° F. These forms of decomposition are completely arrested or prevented by boiling or freezing.

The ferments consist of nitrogenous bodies, such as pepsin, pancreatine, etc., called *soluble ferments;* and of microscopic forms of life, such as the yeast plant, called *organized ferments.*

A small quantity of the ferment is capable of exciting a great deal of chemical action; this is accompanied by no apparent change in the soluble ferment, and only such changes in the organized ferment as are incident to life and reproduction. The ferments probably have the power of exercising catalytic action in causing chemical change in other substances.

The nature of the ferment frequently determines the character of the product formed from a given substance. Lactic acid and alcohol are both obtained from sugar by the action of different ferments.

The soluble ferments, also called *enzymes,* are secreted by organized ferments and by living tissue cells. They exist in the secreting animal cells in an inactive state, called zymogens, which become active on coming in contact with the air, or with acids or alkalies. They are soluble in water or glycerine, and are precipitated from solution by absolute alcohol.

Soluble ferments which break down proteins into simpler forms are termed proteolytic; those which convert amyloses into sugars are called amylolytic; those which change complex to simpler sugars are called glycolytic.

Soluble ferments are found in the vegetable and animal kingdoms, and they generally serve to promote chemical changes which contribute to the nutrition of the plant or animal. Some of the important ferments found in plants are—diastase, from germinating grain; emulsin, from the almond; papain, from the pawpaw tree; and bromelin, from the pineapple. Ferments from animal tissues are—pepsin, pancreatine, ptyalin, invertase.

Organized ferments are living microörganisms, chiefly bacteria, and they are capable of producing both normal and pathological forms of fermentation in the body. Some of the more important members of this class are—the yeast fungus; the Mycoderma Aceti, or mother of vinegar; Oidium Albicans, or

thrush fungus; Bacilli Lactici and Bacilli Butyrici, or bacilli of lactic and butyric acids; putrefying, nitrifying, and pathogenic ferments.

Putrefaction is the breaking up of molecules containing one or more of the elements sulphur, phosphorus and nitrogen in organic combination, and it takes place under the same conditions as fermentation. These elements are converted into hydrogen sulphide, hydrogen phosphide, and ammonia, and impart a disagreeable odor to the putrefying substance.

The products of putrefaction have no value, but many of the bodies formed by fermentation are used in the arts and in medicine.

Fermentation, putrefaction, and decay, or oxidation, all participate in the changes taking place in decomposition of exposed animal matter.

The entrance of pathogenic organized ferments into the living tissues is known as infection when the ferments have established themselves to the detriment of the host. Antiseptics and disinfectants are some of the agents employed to combat the infecting bodies. *Antiseptics* retard the growth and development of infecting organisms. *Disinfectants* destroy the infecting material. *Deodorants* destroy or remove offensive odors.

Action of Nitric Acid on organic bodies results in the formation of three different classes of compounds:

1. The acid unites with organic bases to form salts, or nitrates; an action similar to that seen in inorganic chemistry.

2. Nitro-compounds may be formed, in which the radical NO_2, from nitric acid, enters the organic molecule.

3. Simple oxidation may take place, in which the nitric acid gives up its oxygen to the organic substance.

CLASSIFICATION OF ORGANIC BODIES.

All organic bodies may be regarded as being derived from hydrocarbons, and since the hydrocarbons can be divided into two great groups—fatty and aromatic—we have a corresponding arrangement for their derivatives. 1. *Fatty Compounds* are those derived from methane, or marsh gas, CH_4. 2. *Aromatic Compounds* are those derived from benzene, C_6H_6.

Organic bodies are further arranged in the following groups, for convenience of study, in accordance with chemical composition and structure:

1. **Hydrocarbons** are compounds containing the elements carbon and hydrogen.

Examples: CH_4, Methane; C_2H_6, Ethane.

2. **Alcohols** are hydrocarbon radicals in combination with hydroxyl, OH.

Examples: CH_3OH, Methyl alcohol; C_2H_5OH, Ethyl alcohol.

3. **Aldehydes** are hydrocarbon radicals in combination with COH, formed in the first stage of oxidation of primary alcohols by the removal of hydrogen.

Examples: CH_2O, Methyl aldehyde; C_2H_4O, Ethyl aldehyde.

4. **Ketones** are hydrocarbon radicals in combination with the group CO.

Example: $(CH_3)_2CO$. Dimethyl ketone

5. **Acids** are hydrocarbon radicals in combination with the group, HCO_2, denominated carboxyl.

Example: $CH_3(CO_2H)$. Acetic acid

6. **Ethers** are the oxides of hydrocarbon radicals.

Examples: $(C_2H_5)_2O$, Ethyl ether; $(CH_3)(C_2H_5)O$. Methyl-ethyl ether

7. **Compound Ethers, or Esters,** are the salts formed by the union of hydrocarbon radicals with acid radicals.

Example: $(C_2H_5)C_2H_3O_2$.
Ethyl acetate

8. **Carbohydrates** generally contain six atoms of carbon, or some multiple of six, in combination with hydrogen and oxygen in the proportion to form water. They are aldehydes and ketones of the hexatomic alcohol mannitol.

Examples: Sugars, starch, &c. $C_6H_{10}O_5$.

9. **Amines and Amides** are compounds formed by replacement of the hydrogen of ammonia by alcohol or acid radicals.

Examples: $C_2H_5NH_2$, $C_2H_3ONH_2$.
Ethylamine Acetamide

10. **Cyanogen and its derivatives** contain the radical, CN.

Example: HCN.
Hydrocyanic acid

11. **Diazo and Azo compounds** contain the radical N_2.

Examples: $C_6H_5N_2Cl$, $(C_6H_5)_2N_2$.
Diazo-benzene chloride Azo-benzene

12. **Hydrazines** are formed by replacing hydrogen in the compound, hydrazine, N_2H_4.

Example: $C_6H_5N_2H_3$.
Phenyl hydrazine

13. **Pyridine Bases** are compounds containing nitrogen in the benzene nucleus.

Example: C_5H_5N.
Pyridine

14. **Pyrrole Derivatives** are formed by replacing hydrogen in pyrrole, C_4H_5N.

Example: C_4HI_4N.
Iodol

15. **Alkaloids** are feebly basic substances containing nitrogen. They belong to the group of amines and amides.

Examples: $C_8H_{17}N$, $C_{21}H_{22}N_2O_2$.
Conine Strychnine

16. **Ptomaines** are feebly basic substances, containing nitrogen, formed by the action of bacteria on nitrogenous organic matter.

Example: Cadaverine.

17. **Leucomaines** are nitrogenous basic substances, formed as products of tissue metabolism in the living body.

Examples: Creatine, Adenine.

Compounds of undetermined composition comprise:

1. **Glucosides,** or bodies which when decomposed give glucose as one of the products.

Example: Amygdalin.

2. **Bitter Principles,** of vegetable or animal origin, crystalline and amorphous.

Examples: Aloin, chlorophyll, biliary pigments.

3. **Proteids** containing carbon, hydrogen, oxygen, nitrogen and sulphur, and sometimes other elements.

Examples: Albumen, myosin, casein, &c.

HYDROCARBONS.

Definition. A compound containing carbon and hydrogen as its constituent elements.

Occurrence in Nature. Usually found as a direct or indirect product of vegetable life. They are formed in the tissues of plants by a series of chemical changes from carbon dioxide and water:

$$10CO_2 + 8H_2O = C_{10}H_{16} + 28O.$$

Also produced in nature by the decomposition of vegetable substances in the presence of moisture, and during the formation of coal in the interior of the earth.

Formation of Hydrocarbons by Artificial Means. Carbon and hydrogen do not readily enter into direct chemical union, but the compound acetylene, C_2H_2, can be made by passing

a current of electricity between electrodes of carbon in an atmosphere of hydrogen. The hydrocarbon marsh gas, CH_4, can be made by passing the vapors of carbon bisulphide and water, or hydrogen sulphide, over red-hot metals, as shown by the equations:

$$CS_2 + 2H_2S + 8Cu = 4Cu_2S + CH_4.$$
$$CS_2 + 2H_2O + 6Cu = 2Cu_2S + 2CuO + CH_4.$$

These reactions are of great interest, for they show the possibility of forming organic bodies from the elements, since carbon bisulphide, hydrogen sulphide and water are all easily formed from elementary substances.

Many hydrocarbons are produced by the destructive distillation of organic bodies. Other forms of decomposition of organic bodies sometimes result in the production of hydrocarbons. For example, by heating calcium acetate with sodium hydroxide marsh gas is formed, thus:

$$\underset{\text{Calcium acetate}}{Ca(C_2H_3O_2)_2} + \underset{\text{Sodium hydroxide}}{2NaOH} = \underset{\text{Marsh gas}}{2CH_4} + \underset{\text{Sodium carbonate}}{Na_2CO_3} + \underset{\text{Calcium carbonate}}{CaCO_3}.$$

The hydrocarbons found in nature and most of those produced by artificial means have to be separated from impurities and from each other by fractional distillation, crystallization, and differences in solubility, melting point, and other properties, before the individual members can be studied.

General Properties of the Hydrocarbons. The number of hydrocarbons is very great, and the possible number is almost unlimited on account of the linking power of carbon atoms and the isomeric modifications. They are found in all three states of aggregation, their position in this respect depending upon the proportion of carbon in the molecule, and the molecular weight of the individual compound. Those containing not more than four (4) carbon atoms to the molecule are generally gases, from 4 to 12 liquids, and those having more than 12

carbon atoms are usually solids. All are volatile and colorless when pure. They are usually insoluble in water; soluble in alcohol, ether, bisulphide of carbon and the liquid members of the same group. In chemical properties they are neutral in reaction, and inert. Some are saturated, others unsaturated. Many oxidize in the air.

Classification of Hydrocarbons. The hydrocarbons are classified according to their chemical composition into homologous series, as is shown in the following table:

CLASSIFICATION OF HYDROCARBONS ACCORDING TO CHEMICAL COMPOSITION.[1]

Methane, or Paraffine Series, C_nH_{2n+2}.	CH_4 Methane	C_2H_6 Ethane	C_3H_8 Propane	C_4H_{10} Butane	C_5H_{12} Pentane	C_6H_{14}. Hexane
Ethene Series, or Olefine Series, C_nH_{2n}.		C_2H_4 Ethene	C_3H_6 Propene	C_4H_8 Butene	C_5H_{10} Pentene	C_6H_{12}. Hexene
Ethine Series, or Acetylene Series, C_nH_{2n-2}.		C_2H_2 Ethine, or Acetylene	C_3H_4 Propine, or Allylene	(C_4H_6) (Butine)	C_5H_8 Pentine	C_6H_{10}. Hexine
Ethone Series, C_nH_{2n-4}.			(C_3H_2) (Propone)	(C_4H_4) (Butone)	C_5H_6 Pentone, or Valylene	C_6H_8. Hexone, or Diallylene
Ethune Series, C_nH_{2n-6}.				(C_4H_2) Butune	(C_5H_4) Pentune	C_6H_6. Hexune, or Dipropargyl

THE PARAFFINE, OR METHANE SERIES OF HYDROCARBONS.

The name is derived from some of the higher members of the series which constitute the paraffine of commerce. The members of this group form an homologous series, of the general formula C_nH_{2n+2}. They also form homologous series of derivations, as is shown below:

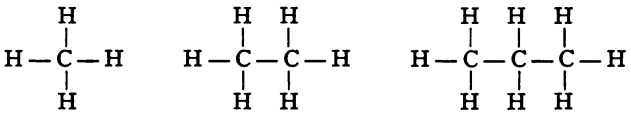
[1] Modification of Dr. Hoffman's classification in using Greek prefixes instead of Latin.

Hydrocarbon.		Alcohol.		Acid.
CH_4	—	CH_4O	—	CH_2O_2.
C_2H_6	—	C_2H_6O	—	$C_2H_4O_2$.
C_3H_8	—	C_3H_8O	—	$C_3H_6O_2$.
C_4H_{10}	—	$C_4H_{10}O$	—	$C_4H_8O_2$.
C_5H_{12}	—	$C_5H_{12}O$	—	$C_5H_{10}O_2$.

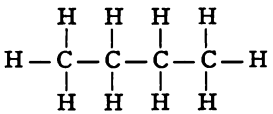
The paraffines show a gradual increase in boiling point, viscidity and specific gravity with increase of molecular weight. The first four members of the series are gases at the ordinary temperature, others are liquids, while some of the higher members are solids. In chemical properties they are neutral, saturated compounds, capable of yielding substitution derivatives by replacement of hydrogen:

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

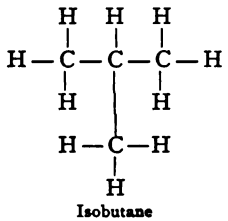
Most of them exist in isomeric modifications showing slight differences in properties, owing to a difference in molecular structure. The first three members are only known in one form, there being only one possible arrangement of the atoms for each, thus:



There are two possible arrangements of the atoms in the molecule for the fourth member, and two varieties of this compound are known, thus:

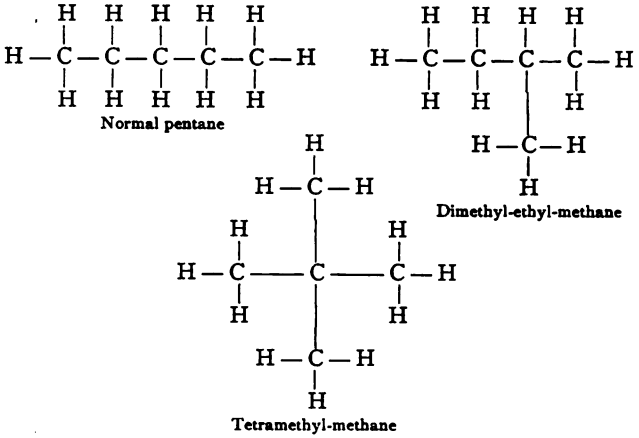


Butane



Isobutane

Three forms are possible for the fifth, and three varieties are known, thus:



In like manner, with advance in the series, there is a constant increase in the number of isomeric forms for each member.

Methane, Marsh Gas, Fire Damp, CH_4.

Formation and Occurrence in Nature. Marsh gas is formed in nature during the process of decay of vegetable matter under water, and rises to the surface of stagnant pools. It is also produced in the formation of coal in the earth. The artificial formation of this gas is accomplished by destructive distillation of non-nitrogenous organic matter, or by action of carbon-bisulphide vapors and steam on heated metallic copper.

Properties. A clear, colorless, odorless, tasteless, combustible gas; density, .8; specific gravity, .559. Under a pressure of 140 atmospheres at 0° it becomes a colorless liquid. When mixed with air it forms the explosive "fire damp" of coal mines.

Marsh gas forms many derivatives by replacement of its hydrogen by other elements or groups of elements, and many

of these derivatives occur in several isomeric forms. In this light, marsh gas may be viewed as the parent substance of many thousands of organic compounds.

The members of the paraffine series of hydrocarbons are formed by replacing hydrogen in each preceding member by the radical, CH_3, thus:

$$CH_3CH_3 = C_2H_6, \quad C_2H_5CH_3 = C_3H_8, \quad C_3H_7CH_3 = C_4H_{10}, \quad \&c.$$

Ethane, or Dimethyl, $CH_3 - CH_3$, or C_2H_6. Found in crude petroleum and in natural gas. It is a clear, colorless, inflammable gas; slightly soluble in water and alcohol.

The artificial preparation of ethane is of interest because it shows the method by which the higher hydrocarbons can be formed. It can be formed by replacing hydrogen in marsh gas with iodine, and acting on the resulting compound with metallic sodium, thus:

$$2CH_3I + 2Na = 2NaI + C_2H_6.$$

The formation of ethane and propane is shown in the following equations, and is of general interest:

$$(CH_3)_2Zn + 2CH_3I = ZnI_2 + 2C_2H_6.$$

$$(CH_3)_2Zn + 2C_2H_5I = ZnI_2 + 2C_3H_8.$$

Coal is derived chiefly from cellulose, and represents the changed remains of vegetable substances which once flourished on the earth's surface. When vegetable matter undergoes decomposition in the absence of air, in the earth, a change takes place which is very similar to that which occurs in destructive distillation. Carbon dioxide, marsh gas and water are given off, and the residue, rich in carbon, remains as coal. Coal consists chiefly of carbon, and besides this element it contains small amounts of hydrogen, oxygen, nitrogen, sulphur, and inorganic salts which represent the ash. As the formation of coal proceeds the proportionate quantity of carbon increases, while the hydrogen and oxygen diminish. Anthracite coal contains the largest percentage of carbon and represents the most complete change from cellulose. Bituminous coal represents an earlier stage of formation and contains a relatively

smaller proportion of carbon, with more of hydrogen and oxygen, than is found in anthracite.

Natural gas is the product of complete decomposition of vegetable and animal matter which has been precipitated from water with inorganic matter during the formation of rocks.

Coal oil, or petroleum is the product of decomposition of organic matter, probably the fats of fish and other aquatic animals, by natural destructive distillation.

Crude petroleum is made up of a mixture of liquid paraffines with solid and gaseous paraffines in solution, and also contains hydrocarbons of other series. These hydrocarbons may be separated from each other by fractional distillation, advantage being taken of differences in the boiling point of the individual members.

Crude petroleum yields a number of useful products. It is first refined by the addition of sulphuric acid, and it is then distilled at different temperatures. The hydrocarbons of low boiling point come over first, consisting of *rhigoline,* B. P. 21°; *benzin, or petroleum ether,* B. P. 50° to 60°, and corresponding to the formula of about C_5H_{12}, C_6H_{14}; *gasoline,* B. P. 75°.

Benzin, or petroleum ether, must not be confounded with benzene (or benzol), the latter being an aromatic hydrocarbon derived from coal tar.

Illuminating oil distills at a temperature of 150° to 250°. If hydrocarbons having a much lower boiling point have not been thoroughly removed in the distillation, they become volatilized when the oil is heated, and form explosive mixtures with air. It is on account of their presence that explosions sometimes occur in the use of illuminating oil.

Mineral machine oil, *liquid and solid vaseline,* or *"petrolatum,"* distill at temperatures approximating 300°. The lubricating oil and liquid vaseline represent different degrees of purity of the same substance, while vaseline represents hydrocarbons of higher molecular weight and boiling point.

Paraffine distills at a temperature of about 350°, and consists of a mixture of the solid hydrocarbons of high molecular weight.

Illuminating Gas is manufactured by destructive distillation of coal. It contains, when first prepared, *hydrogen, methane, ethene, acetylene, nitrogen, ammonia, carbon monoxide, carbon dioxide, hydrogen sulphide, and hydrocyanic acid.* The gas is purified by passing through water and over calcium hydroxide, to remove ammonia, carbon dioxide, hydrogen sulphide and hydrocyanic acid.

The liquid product of the destructive distillation of coal is known as *coal tar,* and contains many useful chemicals, notably, *benzene, aniline, toluene,* and *acetic acid.* Other useful bodies found in coal tar are *carbolic acid, naphthalene* and *paraffine.* Coke is left as the solid residue of the distillation.

THE OLEFINE SERIES OF HYDROCARBONS.

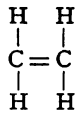
General formula, C_nH_{2n}. The hydrocarbons of the paraffine series are saturated compounds—*i. e.,* they are not capable of forming derivatives by the addition of other elements, and only form them by replacement of some of the atoms in the molecule. The hydrocarbons of this series, the olefines, are capable of forming derivatives by addition of the atoms of other elements to the molecule and they are, therefore, known as unsaturated hydrocarbons. The same is true of the *acetylene* series, and of the *ethone* and *ethune* series.

The members of the olefine series are *ethene, or ethylene,* C_2H_4; *propene, or propylene,* C_3H_6; *butene, or butylene,* C_4H_8; *pentene, or amylene,* C_5H_{10}; *hexene, or hexylene,* C_6H_{12}.

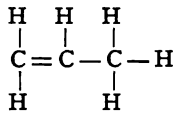
The first member of this series, methene, CH_2, is not known, but the succeeding members as high as $C_{30}H_{60}$ have been obtained. The structure of the members of this series is generally explained by assuming that the carbon atoms are temporarily

doubly linked together, thus permitting them to unite directly with other elements to form addition products.

This structure is well shown in the graphic formulæ:



Ethene



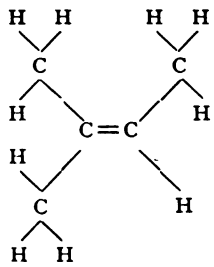
Propene

The olefines occur in nature associated with paraffines in petroleum, and are formed by destructive distillation of fats, waxes, coal and many other substances. They are present, therefore, in illuminating gas, and add greatly to the luminosity of the flame.

In properties they are much like the paraffines, the first three being gases, C_5H_{10} a volatile liquid, and the higher members solids. They are usually soluble in alcohol and ether, and insoluble in water.

Ethene, or ethylene, C_2H_4, is present in illuminating gas. It combines directly with chlorine to form ethylene dichloride, $C_2H_4Cl_2$, an oily liquid, and for this reason is called "olefiant gas" (oil forming), a name which is applied to the series.

Pentene, or Amylene, C_5H_{10}, has been used in medicine under the name "pentol" as an anæsthetic. The isomeric variety known as trimethyl-ethylene is the one used, represented by the graphic formula:



It is formed from amylene hydrate by the action of dehydrating agents.

In properties it is a colorless, volatile, inflammable liquid, boiling at 37° to 38° C. It is soluble in chloroform, ether and alcohol, but insoluble in water.

THE ACETYLENE SERIES OF HYDROCARBONS.

These have the general formula, C_nH_{2n-2}. They are unsaturated hydrocarbons capable of taking up four atoms of univalent elements. Their structure is explained by referring to the graphic formula of acetylene:

$$H-C\equiv C-H.$$

The first five members of this series are given in the table of classification of hydrocarbons.

They are formed by destructive distillation of many organic bodies, and in general properties resemble the members of the olefine series.

Acetylene, C_2H_2, is the most important of these. It is formed in many different ways. Thus, when alcohol, ether or aldehyde are passed through red-hot tubes, acetylene forms. It is also formed by incomplete combustion of coal gas when the flame of the Bunsen burner " strikes back "; when electrical currents are passed between poles of carbon in an atmosphere of hydrogen.

The most common method of preparation is by the action of calcium carbide on water, thus:

$$CaC_2 + H_2O = CaO + C_2H_2.$$

In properties it is a colorless, combustible gas, with an unpleasant odor. It burns with a bright luminous flame.

The unsaturated hydrocarbons of the general formula, C_nH_{2n-4}, *Valylene,* C_5H_6, and *Diallylene,* C_6H_8, have been obtained by destructive distillation of cannel coal and bones.

The terpines, $C_{10}H_{16}$, which have the same general formula, do not belong in this class, for they are probably closely related to the aromatic hydrocarbons.

Of the fatty hydrocarbons in the series, C_nH_{2n-6}, only one is known. This is dipropargyl, C_6H_6, and is of no practical interest. While the formula for dipropargyl corresponds to that for benzene, it must be remembered that the former is a fatty hydrocarbon and, therefore, entirely different from the latter, which is aromatic.

The hydrocarbons of the benzene or aromatic series will be studied after we have considered the derivatives of the fatty series.

HALOGEN DERIVATIVES OF HYDROCARBONS.

Action of Halogens upon Saturated Hydrocarbons. The action in this case consists in replacement of the hydrogen of the hydrocarbon by the halogen atom. Chlorine and bromine are capable of direct action, replacing one or more atoms, and the action is greatly facilitated by presence of light and heat.

Iodine does not act directly, like chlorine and bromine, but the iodine derivatives are obtained by the action of hydriodic acid upon the alcohol derivative of the hydrocarbon. Hydrochloric and hydrobromic acids will also act in the same way—thus:

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Hydrobromic acid}}{HBr} = \underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{Water}}{H_2O}.$$

Action of Halogens upon Unsaturated Hydrocarbons. This action consists in the addition of halogen atoms to the hydrocarbon, or in simple replacement of hydrogen, thus: From C_2H_4 may be formed $C_2H_4Cl_2$, an addition derivative; or, $C_2H_2Cl_2$, a replacement derivative. The action of a halogen acid upon an unsaturated hydrocarbon is represented by the equation:

$$\underset{\text{Ethylene}}{C_2H_4} + \underset{\text{Hydrochloric acid}}{HCl} = \underset{\text{Ethyl chloride}}{C_2H_5Cl}.$$

General Properties of the Halogen Derivatives. Insoluble in water, soluble in alcohol and ether; lower members have an

ethereal odor and sweet taste, and produce insensibility when inhaled.

Methyl Chloride, CH_3Cl. *Preparation.* By heating sodium chloride, sulphuric acid and methyl alcohol:

$$\underset{\text{Sodium chloride}}{2NaCl} + \underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Methyl alcohol}}{2CH_3OH} = \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Water}}{2H_2O} + \underset{\text{Methyl chloride}}{2CH_3Cl}.$$

Properties. A colorless gas, ethereal odor, inflammable; liquefied by pressure of five atmospheres to ethereal liquid. *Used* as a local anæsthetic.

Ethyl Chloride, C_2H_5Cl. *Prepared* like methyl chloride.

Properties. A colorless, mobile, inflammable liquid, boiling at 12°. *Used* largely from glass tubes as local anæsthetic.

Trichlor-Methane, Chloroform, $CHCl_3$. Discovered in 1831 by Liebig.

Preparation. Can be made by the action of chlorine on marsh gas. Usually made by distilling a mixture of bleaching powder, calcium hydroxide and alcohol. The impure product is shaken with sulphuric acid and allowed to stand, when the upper layer is removed and mixed with sodium carbonate, to remove acid, and distilled from calcium oxide, to remove water.

The chemical changes taking place are these:

$$\underset{\text{Ethyl alcohol}}{C_2H_6O} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Ethyl aldehyde}}{C_2H_4O} + \underset{\text{Hydrochloric acid}}{2HCl}.$$

$$\underset{\text{Ethyl aldehyde}}{C_2H_4O} + \underset{\text{Chlorine}}{3Cl_2} = \underset{\text{Chloral}}{C_2HCl_3O} + \underset{\text{Hydrochloric acid}}{3HCl}.$$

$$\underset{\text{Chloral}}{2C_2HCl_3O} + \underset{\text{Calcium hydroxide}}{Ca(HO)_2} = \underset{\text{Calcium formate}}{Ca2HCO_2} + \underset{\text{Chloroform}}{2CHCl_3}.$$

Can be made also by distilling a mixture of acetone and bleaching powder:

$$2(CH_3)_2CO + 3Ca(ClO)_2 = 2CHCl_3 + 2Ca(OH)_2 + \underset{\text{Calcium acetate}}{Ca(C_2H_3O_2)_2}.$$

Properties. Colorless, mobile, diffusible liquid; ethereal odor, burning, sweet taste. Blisters the skin. Specific gravity, 1.476; boiling point, 61°. Dissolves phosphorus, iodine, alkaloids, resins, fats and fatty oils. Liable to decompose by expoure to light with formation of chlorine and hydrochloric acid. Presence of small quantity of alcohol acts as a preservative, and about one per cent. is present in the official article. Not inflammable. *Used* as an anæsthetic. Air must be given with the vapor.

Tests for Purity.

Presence of alcohol indicated by reduced specific gravity; of chlorine or hydrochloric acid, by shaking with water and adding silver nitrate to the latter, when white precipitate forms. Aldehydes indicated by brown color with caustic potash. Should not be colored by sulphuric acid. Should leave no residue upon evaporation.

Tests for Presence.

1. Paper moistened with chloroform and ignited gives flame with green mantle, and vapors of hydrochloric acid.

2. Heated with alcoholic solution of caustic potash and aniline, a sickening odor is given off (benzo-isonitril).

3. Vapors passed through red-hot glass tube decomposed into chlorine, carbon and hydrochloric acid.

Tri-bromo-Methane, Bromoform, $CHBr_3$. *Prepared* by adding bromine to a solution of caustic potash in methyl alcohol until the color no longer disappears, and purified by distilling from calcium chloride.

Properties like chloroform. Specific gravity, 2.808; boiling point, 148°. *Used* as antispasmodic in whooping-cough.

Tri-iodo-Methane, Iodoform, CHI_3. *Prepared* by heating together water, ethyl alcohol, potassium carbonate and iodine until brown color of iodine disappears. The iodoform crystals deposit upon standing.

$C_2H_5OH + 3K_2CO_3 + 4I_2 = CHI_3 + KHCO_2 + 5KI + 2H_2O + 3CO_2$.

Properties. Small, lemon-yellow, shining crystals, of disagreeable odor, sweetish taste. Insoluble in water, soluble in alcohol, ether and oils. Contains 96 per cent. of iodine. *Used* as an antiseptic.

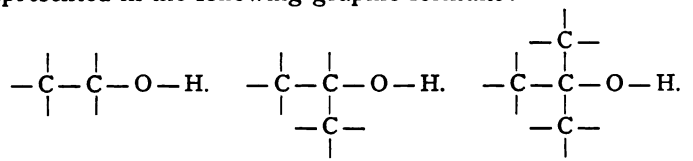
Test for iodoform: Odor.

ALCOHOLS.

Alcohols are formed by replacement of the hydrogen of hydrocarbons by the radical, hydroxyl (OH). They are, therefore, hydroxides of hydrocarbon residues, and form series to correspond with the series of hydrocarbons. Alcohols are monatomic, diatomic, triatomic, tetratomic, &c., according to the number of hydrogen atoms thus replaced—one, two, three, four, &c. Heptatomic alcohols, those containing seven hydroxyl radicals, are the highest that have been found in nature.

Alcohols are further classed as *primary, secondary* and *tertiary.* A primary alcohol is one in which the hydroxyl is attached to a carbon atom which, in turn, is attached to a *single* other carbon atom. A secondary alcohol has its hydroxyl united with a carbon atom which is attached to *two* other carbon atoms. A tertiary alcohol has its hydroxyl united with a carbon atom which is attached to *three* other carbon atoms.

The structure of primary, secondary and tertiary alcohols is represented in the following graphic formulæ:



Primary Secondary Tertiary

The isomeric forms of hydrocarbons give isomeric alcohols.

Occurrence in Nature. Alcohols are not found free in nature, but generally occur as salts with acids, in the form of compound ethers in fats and essential oils.

General Methods of Preparation:

1. They may be formed by the action of strong alkalies upon compound ethers. This chemical change is referred to in a general way as saponification, and is represented in the equation:

$$\underset{\text{Ethyl acetate}}{C_2H_3C_2H_3O_2} + \underset{\substack{\text{Potassium}\\\text{hydroxide}}}{KOH} = \underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Potassium acetate}}{KC_2H_3O_2}.$$

$$CH_3Cl + KOH = CH_3OH + KCl.$$

2. By the action of moist silver oxide on the chloride or bromide of the hydrocarbon residue, thus:

$$C_2H_5Cl + AgOH = AgCl + C_2H_5OH.$$

3. Many may be formed by fermentation, and some by destructive distillation.

General Properties. The alcohols of the lower members of the series are thin, volatile liquids, soluble in water; the higher ones are oily, volatile liquids, but insoluble in water; while the highest alcohols are solid, crystalline, non-volatile and insoluble in water. The lower members have a burning taste and an aromatic odor. The highest members are odorless and tasteless. They are usually colorless when pure.

Though alcohols are neutral bodies, yet the hydrogen of the hydroxyl may be replaced by strongly basic metals like potassium or sodium (CH_3ONa, sodium methylate), and the oxygen may be replaced by sulphur. The compounds formed by replacement of the oxygen of the hydroxyl of alcohols by sulphur are called *mercaptans* (from *mercurio aptum,* because of their affinity for mercuric oxide), or, more properly, *hydrosulphides.* These are formed by the action of potassium hydrosulphide upon the chloride of the hydrocarbon radical, thus:

$$CH_3Cl + KHS = KCl + CH_3SH.$$

Methyl Alcohol, Wood-Spirit, Wood-Naphtha, CH_3OH.

Methyl alcohol *occurs in nature* as methyl salicylate, or oil of wintergreen, in *Gaultheria procumbens.*

Preparation. It is obtained by destructive distillation of wood. The liquid product of distillation is treated with calcium hydroxide to neutralize acetic acid, and distilled; and the distillate, containing methyl alcohol, is purified by repeated distillation. It is further purified by adding oxalic acid to form the crystalline oxalate of methyl, which is dried and decomposed by boiling with ammonia.

Properties. A clear, colorless, inflammable liquid, boiling at 66°; specific gravity 0.812. It is miscible with water, and dissolves fats, resins and camphors. It has an aromatic odor, a burning taste. It acts as a poison when taken internally.

The impure methyl alcohol has a nauseous odor and taste, and a ten per cent. solution in ethyl alcohol is used as *methylated spirit.*

Methyl alcohol is sometimes called *carbinol,* and its hydrocarbon derivatives are referred to as carbinols. (Methyl-carbinol, CH_3CH_2OH.)

Ethyl Alcohol, Alcohol, C_2H_5OH. *Occurs in nature* as butyric ether, and in diabetic urine.

Preparation. (a) *Theoretical Methods:*

1. From ethane, by treating it with chlorine to form ethyl chloride, and decomposing this with caustic potash, thus:

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl,$$

$$C_2H_5Cl + KOH = C_2H_5OH + KCl.$$

2. By the action of sulphuric acid upon ethylene, and decomposing the resulting ethyl-sulphuric acid with water, thus:

$$C_2H_4 + H_2SO_4 = C_2H_5HSO_4,$$

$$C_2H_5HSO_4 + H_2O = C_2H_5OH + H_2SO_4.$$

(b) *Practical Method:* By the alcoholic fermentation of sugar, in which the sugar (usually glucose) is split up into car-

bon dioxide and ethyl alcohol, under the influence of a ferment (yeast). Other alcohols, homologous with ethyl alcohol, are formed at the same time, as "fusel oil." The formation of alcohol from glucose is represented by the equation:

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2.$$

A diluted solution of glucose is allowed to ferment, and by repeated distillation of the liquid an alcohol containing about 14 per cent. of water can be obtained. The remaining water is removed by mixing with calcium oxide, allowing to stand and then distilling.

Properties. Pure alcohol is a clear, colorless, mobile, inflammable liquid, aromatic odor, and burning taste. Its boiling point is 78.5°, specific gravity 0.79, and solidifies at — 130°. It mixes with water in all proportions with evolution of heat and contraction in volume. The coagulating and preservative action of alcohol for animal substances is largely due to its affinity for water. Alcohol is a solvent for many substances, such as fats, resins, essential oils, alkaline hydroxides, and calcium chloride.

The presence of water in alcohol may be shown by mixing with benzene. This mixture shows a turbidity if the alcohol contain more than 3 per cent. of water; if less, it is clear. Water may be removed by adding anhydrous copper sulphate, or heated potassium carbonate.

"*Absolute alcohol*" of the U. S. P. contains not more than one per cent. of water; "*alcohol*" contains 92.3 per cent. by weight, or 94.9 per cent. by volume, specific gravity 0.816 at 15.6° C.; "*diluted alcohol*" is made by mixing equal volumes of water and alcohol. All of these are official.

Pure alcohol acts as a poison but when diluted it is a stimulant and intoxicant, reducing the body temperature .5° to 2°.

Tests.

1. Dissolve crystals of iodine in alcohol and add solution of caustic potash until the brown color disappears. Upon standing, crystals of iodoform will be deposited.

2. Add sulphuric acid, heat, and then add more alcohol. The aromatic odor of ethyl sulphate is developed.

3. Add a crystal of potassium dichromate and a few drops of sulphuric acid. Upon heating, the odor of ethyl aldehyde develops and the liquid turns green.

Alcoholic Liquors are manufactured by fermentation of liquids containing a fermentable sugar, such as glucose and maltose. Various grains are used for this purpose, and in them the starch is utilized by converting it into maltose by germination. The grain is first caused to sprout, whereby diastase converts starch into the fermentable sugar maltose, and it is then heated to a sufficiently high temperature to stop further growth. From the "malted grain" an infusion is made, known as "wort," and this is subjected to fermentation by the action of yeast (chiefly *Saccharomyces cerevisiæ*).

These liquors may be divided into the ***undistilled*** and the ***distilled.***

The undistilled liquors contain, besides alcohol, many non-volatile organic and inorganic substances, and some of these have a slight nutritive value; for example, the nitrogenous constituents of beer. Members of this class are: *Wines,* formed by fermentation of grape juice. *Light wines,* as *claret,* usually contain from 5 to 12 per cent. of alcohol; ***heavy wines,*** as *sherry* and *port,* from 19 to 25 per cent. *Beer,* usually made by fermentation of wort of barley to which hops have been added, contains from 2 to 6 per cent. of alcohol. *Porter* and *stout* are representatives of this class containing the highest per cent. of alcohol.

Distilled liquors contain only volatile constituents, chiefly alcohol, with some ethers, compound ethers and coloring matters. They usually have from 47 to 55 per cent. of alcohol.

Brandy is made by distillation of French wines. Often made from substitutes, however. *American whiskey,* made by distilling fermented wort of corn or rye; *Irish whiskey,* from potatoes; *Scotch whiskey,* from barley; *rum,* from molasses; *arrack,* from rice. *Gin* is grain spirit flavored with juniper berries.

Fusel Oil is a mixture of *propyl, butyl* and *amyl alcohols,*

C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$.

It is formed during the fermentation of grain or potatoes in the manufacture of spirituous liquors, and comes over at the last of the distillation.

Properties. A clear, colorless, oily liquid; penetrating, aromatic odor; burning, nauseous taste; insoluble in water, soluble in alcohol. *Amyl alcohol* may be obtained from fusel oil by fractional distillation. It is much like fusel oil in properties, and is converted into valerianic acid by oxidation.

Glycerin, $C_3H_5(OH)_3$. Triatomic propyl alcohol.

Occurrence in nature in the form of true fats as compound ethers with fatty acids.

Prepared by the action of superheated steam or caustic alkalies upon fats. In the latter case the alkali combines with fatty acid to form soap, and glycerin is set free, thus:

$$\underset{\text{Olein}}{C_3H_5(C_{18}H_{33}O_2)_3} + 3\underset{\text{Caustic potash}}{KOH} = 3\underset{\substack{\text{Potassium}\\\text{oleate, soap}}}{KC_{18}H_{33}O_2} + \underset{\text{Glycerin}}{C_3H_5(OH)_3}.$$

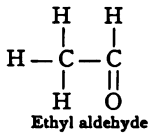
Properties. A clear, colorless, thick, sweet liquid; hygroscopic; soluble in water and alcohol; specific gravity, 1.246. It cannot be volatilized without decomposition, but can be distilled when heated with water or in presence of steam. Glycerin is a good solvent for many organic and inorganic bodies. It forms *glycerites. Boroglycerin,* $C_3H_5BO_3$, a compound of glycerin with boric acid.

Tests.

1. Should not turn dark with sulphuric acid, and when the mixture is heated gives the irritating odor of acrolein.
2. Should give no red color with Fehling's solution; absence of glucose.
3. Heated on platinum foil, should burn without residue.
4. Imparts green color to flame from borax bead.

ALDEHYDES.

Aldehydes contain the radical, HCO, in combination with hydrocarbon residues, thus:



Ethyl aldehyde

Aldehydes are formed by incomplete oxidation of primary alcohols, whereby hydrogen is removed; further oxidation would result in the formation of an acid, thus:

$$\underset{\text{Ethyl alcohol}}{C_2H_6O} + \underset{\text{Oxygen}}{O} = \underset{\text{Water}}{H_2O} + \underset{\text{Ethyl aldehyde}}{C_2H_4O},$$

$$\underset{\text{Ethyl aldehyde}}{C_2H_4O} + \underset{\text{Oxygen}}{O} = \underset{\text{Acetic acid}}{C_2H_4O_2}.$$

The name of the aldehyde is derived from the alcohol whence it comes, and also from the acid it would form by further oxidation, thus: Ethyl alcohol when oxidized forms an aldehyde, and this aldehyde by further oxidation forms acetic acid; the name of the aldehyde, in this case, is ethyl aldehyde, or acetic aldehyde. Few of the aldehydes have more than scientific interest. Formic aldehyde and acetic aldehyde are the ones used in medicine.

Formic Aldehyde, Formaldehyde, Methyl Aldehyde, CH_2O, (H.CHO) is prepared by passing the vapors of methyl alcohol and air over heated spiral of copper or platinum and carefully condensing. This method of preparation gives a mixture of aldehyde and alcohol.

Formic aldehyde may be obtained pure by heating dry calcium formate, as shown in the following equation:

$$\underset{\text{Calcium formate}}{Ca(HCO_2)_2} = \underset{\text{Formic aldehyde}}{CH_2O} + \underset{\text{Calcium carbonate}}{CaCO_3}.$$

Properties. Formic aldehyde is a clear, colorless gas, having a pungent odor, and condensible to a liquid which boils at $-21°$. It is soluble in water or alcohol, and is used extensively as a disinfectant and antiseptic.

Solution of Formaldehyde, U. S. P., is "an aqueous solution, containing not less than 37 per cent., by weight, of absolute formaldehyde."

Paraformaldehyde, $C_3H_6O_3$, is a polymeric form of methyl aldehyde. When a solution of formic aldehyde in methyl alcohol is slowly evaporated, paraformaldehyde separates in crystals. Paraformaldehyde is largely used as a disinfectant by heating, to convert it into gaseous formic aldehyde.

Acetic Aldehyde, Ethyl Aldehyde, C_2H_4O. (CH_3CHO.) *Prepared* by oxidation of ethyl alcohol by dichromate of potash and sulphuric acid and distilling.

Properties. Neutral, colorless liquid; strong, peculiar odor; miscible with water and alcohol; boiling point 21°. Strong tendency to unite with other bodies—hydrogen to form alcohol, oxygen to form acetic acid. Molecules unite with each other to form polymeric modification. A strong reducing agent.

Paraldehyde, $C_6H_{12}O_3$. A polymeric modification of the above. *Produced* by adding a few drops of sulphuric acid to ethyl aldehyde.

Properties. A solid, crystalline mass below 10.5°; a clear, colorless liquid above that point; peculiar odor, disagreeable taste, soluble in 8.5 parts water, boils at 124°. *Used* as hypnotic in *elixir of paraldehyde.*

Trichloraldehyde, Chloral, C_2HCl_3O. ($CCl_3.CHO$.) This compound is formed by replacement of three hydrogen atoms in ethyl aldehyde by chlorine.

Preparation. By passing a stream of dry chlorine gas through ethyl alcohol to saturation. The liquid to be kept cool at first and gradually heated to the boiling point as the operation proceeds. Separates into two layers; the lower layer removed, shaken with sulphuric acid, distilled and mixed with calcium oxide and again distilled; that coming over between 94° and 99°, collected. Chemical changes represented in the equation:

$$C_2H_6O + Cl_2 = C_2H_4O + 2HCl.$$

$$C_2H_4O + 3Cl_2 = C_2HCl_3O + 3HCl.$$

Properties. A clear, colorless, oily liquid; acrid odor and caustic taste; specific gravity 1.5, boiling point 95°.

Chloral Hydrate (U. S. P.), $C_2HCl_3O.H_2O$. *Prepared* by adding water to chloral.

Properties. Colorless, crystalline solid, aromatic, agreeable odor, pungent taste, freely soluble in all the common solvents. Forms a liquid when mixed with camphor or carbolic acid; it melts at 58°.

Tests.

1. Heated with caustic potash gives odor of chloroform:

$$\underset{\text{Chloral}}{C_2HCl_3O} + KOH = \underset{\text{Potassium formate}}{KHCO_2} + \underset{\text{Chloroform}}{CHCl_3}.$$

2. Heated with silver nitrate and ammonia water gives silver mirror.

Sulphur Derivatives of Alcohols. Mercaptans, or hydrocarbon hydrosulphides are formed by replacement of oxygen of the hydroxyl of alcohols by sulphur (C_2H_5HS). These compounds when oxidized form acids, known as sulphonic acids. Thus: When ethyl hydrosulphide, C_2H_5HS, is acted on with nitric acid, it forms *ethylsulphonic acid*, $C_2H_5HSO_3$, by union with three oxygen atoms. The radical of this acid is $C_2H_5SO_2$, known as ethylsulphonyl, and can replace hydrogen in hydrocarbons to unite with the basic residue.

Sulphonal, $C(CH_3)_2(C_2H_5SO_2)_2$, is a compound formed by replacement of two hydrogen atoms of marsh gas by the radical ethylsulphonyl, and the two remaining hydrogen atoms by the radical methyl, CH_3. Its chemical name would therefore be dimethyl-diethylsulphonylmethane.

Prepared by action of ethyl-mercaptan upon dimethyl-ketone, thus:

$$(CH_3)_2CO + 2C_2H_5SH = (CH_3)_2C(C_2H_5S)_2 + H_2O,$$

the product is then oxidized by potassium permanganate, thus:

$$(CH_3)_2C(C_2H_5S)_2 + 2O_2 = \underset{\text{Sulphonal}}{(CH_3)_2C(C_2H_5SO_2)_2}.$$

Properties. Colorless, odorless, tasteless crystals; soluble in 20 parts hot water, 100 parts cold water; soluble in ether, chloroform and benzene.

Trional, *Diethylsulphonyl-methyl-ethyl-methane,* $CH_3C_2H_5C(C_2H_5SO_2)_2$. *Made* by the action of ethyl mercaptan on methyl-ethyl-ketone.

Properties. Colorless, lustrous, odorless crystals, soluble in hot water, alcohol and ether.

Tetronal, $(C_2H_5)_2C(C_2H_5SO_2)_2$. A similar compound in chemical and therapeutic nature.

KETONES.

Ketones are compounds formed by replacement of hydrogen in hydrocarbons by the bivalent radical, CO, or carbonyl.

By oxidation of primary alcohols aldehydes are formed. A primary alcohol containing the radical,—CH_2OH, when oxidized has two of its hydrogen atoms removed and becomes —COH; while on the other hand a secondary alcohol containing CH.OH, when oxidized, loses two hydrogen atoms, and becomes >CO, the radical characteristic of ketones.

The aldehydes represent bodies which result from the incomplete oxidation of primary alcohols, and further oxidation forms the corresponding acid; while ketones represent the first products of oxidation of secondary alcohols, any further oxidation resulting in the decomposition of the molecule, thus:

$$C_2H_4O + O = C_2H_4O_2.$$

$$(CH_3)_2CO + O_3 = C_2H_4O_2 + CO_2 + H_2O.$$

Ketones are not affected by weak oxidizing agents, but require for their oxidation the more powerful ones, like chromic acid.

Dimethyl Ketone, Acetone, $(CH_3)_2CO$, is found in small amount in the blood, in the urine and secretions. The amount in the urine is increased in diabetes mellitus.

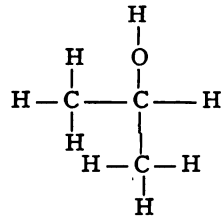
Formed by the distillation of sugar, gums and cellulose.

Preparation. By the dry distillation of calcium acetate:

$$Ca(C_2H_3O_2)_2 = CH_3CH_3CO + CaCO_3.$$

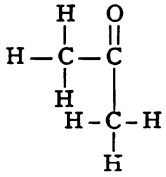
Properties. A clear, colorless liquid, of agreeable ethereal odor; soluble in water, ether and alcohol. Sodium amalgam

reduces it to isopropyl alcohol, from which it may be said to be theoretically derived.



or C_3H_7OH, *Isopropyl alcohol.*

By removal of two atoms of hydrogen from the above, we have:



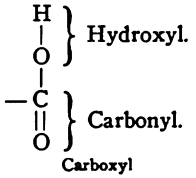
or CH_3COCH_3, *Acetone.*

Acetone is used as a solvent for resins, and for the manufacture of chloroform.

ORGANIC ACIDS.

Definition and Constitution. Compounds formed by replacement of hydrogen of hydrocarbons by the radical carboxyl, HCO_2. The acids are monobasic, dibasic and tribasic, &c., according to the number of hydrogen atoms so replaced —one, two, three, &c.

Carboxyl contains the replaceable hydrogen of the acid, and consists of hydroxyl, OH, and carbonyl, CO. Its structure is represented by the graphic formula:



The organic acids form homologous series corresponding to the series of hydrocarbons from which they are derived.

Occurrence in Nature. Organic acids usually occur in vegetable and animal tissues in combination with bases, or in a free state. They are often found combined with metals in the form of salts, and they sometimes occur with alcohol radicals as compound ethers.

Many of these acids are found free, such as citric acid, in lemon juice; tartaric acid, in the grape and strawberry; oxalic acid, in sorrel; formic acid, in ants; and uric acid, in the flesh-eating animal.

Formation:

1. By oxidation of alcohols, forming first the aldehyde and then the acid.

2. By the action of alkalies on compound ethers to form an alkaline salt of the acid, and then decomposing the salt with a stronger acid.

3. By destructive distillation.

4. By fermentation.

General Properties. They have the properties of inorganic acids as regards taste, reaction and formation of salts; but in the higher members of the series these properties gradually disappear. The lower members of the series are usually colorless liquids of considerable odor, taste, acid reaction and frequently volatile. The higher members become solids without odor, taste, volatility or acid character.

The oxygen of the organic acid is capable of being replaced by sulphur in many cases, and the result of this reaction is the formation of a compound known as a thio-acid, in reference to the sulphur atom. An example of this sort of change can be found in the case of acetic acid, whose chemical formula is $C_2H_4O_2$. When a part of the oxygen is replaced in this acid by sulphur we have an acid whose name is thio-acetic acid, and whose formula is C_2H_4OS.

The Anhydride of an organic acid is formed by removal of one molecule of water from two molecules of the acid, thus:

$$2C_2H_4O_2 - H_2O = (C_2H_3O)_2O + H_2O.$$

The radical of an organic acid may be viewed as that which is left after removal of OH, the acid being an hydroxide of this radical, and the anhydride being an oxide.

1. **Monobasic Fatty Acids, General Formula,** $C_nH_{2n}O_2$.

Formed from primary monatomic alcohols by oxidation.

Formic Acid, $H.HCO_2$. Found in nature in ants, stinging nettle and fir cones.

Preparation. As sodium formate, by action of moist carbon monoxide on dry sodium hydroxide at 200°:

$$CO + NaOH = NaHCO_2.$$

By oxidation of methyl alcohol. By heating oxalic acid with glycerine, thus:

$$C_3H_5(OH)_3 + H_2C_2O_4 = C_3H_5(OH)_2HCO_2 + CO_2 + H_2O.$$

$$C_3H_5(OH)_2HCO_2 + H_2O = C_3H_5(OH)_3 + H_2CO_2.$$

Properties. A clear, colorless liquid, penetrating odor, strongly acid. It is a strong reducing agent, and unites with inorganic bases to form salts. These formates are soluble, except the lead and mercurous salts. The acid, when diluted, acts as a powerful antiseptic; but when concentrated, produces painful blisters on the skin.

Acetic Acid, $H.C_2H_3O_2$. Known to the Ancients as vinegar; to the Alchemists in a purer and more concentrated form.

Occurrence in Nature. Partly free and partly combined with potassium and calcium in plant juices and in perspiration.

Preparation. By oxidation of alcohol and by destructive distillation of wood.

Formed from alcohol by pouring diluted spirit over shavings contained in open casks with holes in the sides for free circu-

lation of air. The acetic ferment, "mother of vinegar," facilitates the oxidation.

Formed from wood by taking the liquid product of destructive distillation, neutralizing with milk of lime, and to the resulting calcium acetate dilute sulphuric acid is added, when the liberated acetic acid is distilled off. Called pyroligneous acid when obtained from this source, and impure.

Properties. When pure, a strongly acid liquid; pungent odor; blisters the skin; solid below 15°; boils at 118°; specific gravity, 1.056; miscible with water, alcohol and ether; forms acetates. The pure acid known as *glacial acetic acid. Acetic acid* U. S. P. contains 36 per cent., and *diluted acetic acid* contains 6 per cent.

The specific gravity of acetic acid cannot be used to determine its strength, since an acid containing 78 per cent. has the highest, 1.074, and an addition of either water or acetic acid will lower the specific gravity.

Ammonium Acetate, $NH_4C_2H_3O_2$. Generally used in solution as "Spirit of Mindereris," which is made by saturating dilute acetic acid with ammonium carbonate.

Ferric Acetate, $Fe_2(C_2H_3O_2)_6$. Made by dissolving ferric hydroxide in acetic acid, and used in solution as *liquor ferri acetatis.* A reddish-brown liquid.

Potassium Acetate, $KC_2H_3O_2$; **Sodium Acetate,** $NaC_2H_3O_2.3H_2O$; **Zinc Acetate,** $Zn(C_2H_3O_2)_2.2H_2O$: Made by dissolving the carbonates of the metals in acetic acid and crystallizing. All three, white soluble salts.

Lead Acetate, $Pb(C_2H_3O_2)_2.3H_2O$. *Sugar of lead.* Made by dissolving lead oxide in diluted acetic acid and crystallizing.

Properties. Shining, transparent, colorless crystals; sweetish, astringent, metallic taste. Soluble in water and to some extent in alcohol; efflorescent in dry air and absorbs carbon dioxide by exposure. Turbidity of solution due to presence of

oxide in the salt which forms carbonate with carbonic acid of impure water, or due to presence of carbonate in the salt; cleared by addition of acetic acid.

Goulard's Extract, solution of subacetate of lead. Made by boiling a mixture of lead acetate and oxide with water, when a basic, or sub-acetate ($Pb(C_2H_3O_2)2PbO$) is formed, and enters into solution. Contains 25 per cent. *Diluted lead water* contains 1 per cent.

Cupric Acetate, $Cu(C_2H_3O_2)_2.H_2O$. Made by dissolving copper carbonate in acetic acid and crystallizing.

Properties. Green, prismatic crystals, soluble in water. *Verdigris* is a basic cupric acetate, $Cu(C_2H_3O_2)_2CuO$, made by the action of dilute acetic acid and air on metallic copper. *Paris green* is an impure cupric aceto-arsenite, made by boiling verdigris with arsenous oxide.

Tests for Acetates.

1. Neutral solutions of acetates turn deep-red on adding ferric chloride.

2. Acetates heated with sulphuric acid give odor of acetic acid.

3. Heated with sulphuric acid and ethyl alcohol, give odor of acetic ether.

Butyric Acid, $H.C_4H_7O_2$. Normal butyric acid found in combination with glycerine in butter, also in cod liver oil and croton oil. Found free in rancid butter, sweat, and cheese. *Formed* by fermentation of lactic acid, or of albumenoids.

Properties. Colorless liquid, disagreeable, rancid odor, soluble in water, boiling at 163°.

Valerianic Acid, $H.C_5H_9O_2$. Found in valerian and angelica root. *Prepared* by oxidation of amyl alcohol, by sulphuric acid and potassium bichromate:

$$C_5H_{11}OH + O_2 = C_5H_{10}O_2 + H_2O.$$

Properties. Colorless, oily liquid, strong, disagreeable odor; boils at 175°; soluble in alcohol, slightly soluble in water. Forms valerianates.

Valerianate of ammonium, of zinc, of quinine and of iron are used in medicine. These are white salts, except the iron valerianate, which is brown. Ammonium valerianate is soluble in water; the others insoluble.

Caproic acid, $H.C_6H_{11}O_2$, and **Caprylic acid,** $H.C_8H_{15}O_2$, the next members of the series, are found in butter. Made from goat's milk (whence the name), cheese and cocoanut oil.

Other acids of the series are: **Pelargonic acid,** $H.C_9H_{17}O_2$; of *Pelargonium roseum;* **Lauric acid,** $H.C_{12}H_{23}O_2$, of spermaceti; **Myristic acid,** $H.C_{14}H_{27}O_2$, of butter and spermaceti.

Palmitic Acid, $HC_{16}H_{31}O_2$. Found in solid fats in combination with glyceryl as *palmitin.* Forms a white insoluble solid, fusing at 60°.

Margaric Acid, $H.C_{17}H_{33}O_2$. Formerly supposed to be present in natural fats. Made only by synthetic means.

Stearic Acid, $H.C_{18}H_{35}O_2$. Occurs in natural fats in combination with glyceryl as *stearin. Properties.* Hard, white, odorless, tasteless solid; insoluble in water, soluble in hot alcohol and ether; melts at 69.2°.

2. Monobasic Fatty Acids, General Formula, $C_nH_{2n-2}O_2$.

These acids are derivatives of the olefine or unsaturated hydrocarbons. The lowest members are only obtained synthetically; the higher ones are found in animal and vegetable fats. The only member of this series of any practical interest is oleic acid.

Oleic Acid, $H.C_{18}H_{33}O_2$. *Occurs in nature* as oleate of glyceryl, or olein, in natural liquid fats. *Prepared* by boiling olive oil with caustic potash, to form potassium oleate, and liberating the oleic acid from this salt by action of tartaric acid.

Properties. Colorless, odorless, tasteless, neutral liquid;

forms crystals when cooled to near 0° ; insoluble in water, but soluble in other common solvents; turns brown by exposure. Specific gravity of oleic acid is 0.895.

This acid forms oleates with basic substances, some of which are used in medicine—*oleate of mercury, lead, veratrine, zinc.*

3. Monobasic Fatty Acids, General Formula, $C_nH_{2n-4}O_2$.

The acids of this series correspond to the acetylene series of hydrocarbons. In this group is found:

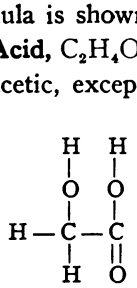
Linoleic Acid, $H.C_{18}H_{31}O_2$. *Found* in combination with glyceryl in linseed oil.

Properties. A yellow liquid, which rapidly solidifies in air.

Organic Acids Derived from Diatomic and Higher Alcohols.

In formation of acids by oxidation of alcohols containing more than one hydroxyl radical, sometimes only a part of the hydroxyl is changed into an acid radical, and the resulting compound partakes of the nature of an alcohol, as well as an acid, because of the remaining alcoholic hydroxyl. For example, the diatomic alcohol, ethylene glycol, $HOH_2C—CH_2OH$, may be oxidized into glycollic acid, $HOH_2C—COOH$. This acid is said to be diatomic; referring to the number of hydroxyl groups, and monobasic; referring to the number of carboxyls. Its graphic formula is shown below.

Glycollic Acid, $C_2H_4O_3$. A monobasic, diatomic acid. Same formula as acetic, except that it contains OH in place of H. Thus:



Hydroxy-acetic acid.

Partakes of the nature of an alcohol and an acid because of alcoholic hydroxyl.

Found in unripe grapes and leaves of wild vine.

Properties. Colorless needles, soluble in water, alcohol and ether.

Lactic Acid, $HC_3H_5O_3$, or $C_2H_4(OH)COOH$. *Occurs in nature* in plant juices, in sauerkraut, gastric juice and gray matter of brain.

Produced by the "lactic fermentation of sugar."

Prepared by mixing sugar, in solution, with putrid cheese, milk and chalk, and digesting for several weeks at temperature of 30°. The resulting calcium lactate purified by crystallization, and decomposed by oxalic acid.

Properties. Official acid has 75 per cent. of pure acid; a colorless, syrupy liquid, odorless, of acid taste; specific gravity 1.206. It absorbs moisture from the air, and is soluble in water, alcohol and ether. *Sarcolactic acid is a form of lactic acid found in muscle tissues.*

Ferrous Lactate, $Fe(C_3H_5O_3)_2.3H_2O$. Made by dissolving iron, as filings, in lactic acid.

Pale, greenish-white crusts, or needle-shaped crystals; peculiar odor, sweetish taste, soluble in water.

Strontium Lactate, $Sr(C_3H_5O_3)_2.3H_2O$. Made by dissolving strontium carbonate in lactic acid. A white, granular, crystalline powder; bitter, saline taste; soluble in water.

Oxalic Acid, $H_2C_2O_4.2H_2O$. *In chemical structure* this acid consists of two carboxyl groups linked together; it is diatomic and dibasic.

Occurrence in Nature in many plants as potassium or calcium salt. Produced by oxidation of many organic bodies by nitric acid; as sugar, starch, cellulose, &c.

Preparation. By heating sawdust and caustic potash to 250°, dissolving the resulting potassium oxalate in water, adding calcium hydroxide and decomposing the precipitated calcium oxalate with sulphuric acid.

Properties. The acid crystallizes in large, prismatic crystals,

with 2 molecules of water, and is soluble in water and alcohol. It as a strong reducing agent, decolorizes solution of potassium permanganate, and acts as a poison. *Antidote:* A salt of calcium.

Cerium Oxalate, $Ce_2(C_2O_4)_3.9H_2O$, is used in medicine as a white, insoluble, granular, tasteless powder.

Salt of Sorrel is the acid potassium oxalate, or this compound in union with oxalic acid. It is used to remove ink-stains and to bleach straw, and is poisonous like oxalic acid.

Tests for Oxalates.

1. Heated with sulphuric acid they give off CO and CO_2.
2. Silver nitrate gives white precipitate of silver oxalate.
3. Neutral solutions with calcium chloride give white precipitate, insoluble in acetic, soluble in hydrochloric acid.

Malic Acid, $H_2C_4H_4O_5$, or $CH_2.CHOH(COOH)_2$. A dibasic, triatomic acid, found extensively in the vegetable kingdom in unripe apples, quinces, grapes, &c. It forms deliquescent, needle-shaped crystals, soluble in water and alcohol.

Tartaric Acid, $H_2C_4H_4O_6$, or $(CHOH)_2(COOH)_2$. A dibasic, tetratomic acid. This acid occurs in four *stereo-isomeric* varieties. *Dextro-tartaric* acid turns the plane of polarized light to the right, and is the usual form of the acid.

Occurrence in Nature. Partly free and partly in combination with calcium and potassium in the juices of fruits. Abundant in grape juice as potassium acid tartrate, which is deposited in wine casks as "argol" during fermentation.

Preparation. By acting on argol with calcium carbonate and then calcium chloride, to form calcium tartrate, and decomposing this salt with sulphuric acid, to form calcium sulphate and tartaric acid; the latter is then crystallized from solution. The chemical changes are represented by the equations:

$$2KHC_4H_4O_6 + CaCO_3 = CaC_4H_4O_6 + K_2C_4H_4O_6 + H_2O + CO_2,$$
$$K_2C_4H_4O_6 + CaCl_2 = CaC_4H_4O_6 + 2KCl.$$

Properties. Colorless, transparent, prismatic crystals, or white powder; agreeable, sour taste; soluble in water and alcohol; melts at 135°.

Potassium Bitartrate, $KHC_4H_4O_6$. (*Cream of tartar.*)

Prepared by purification of argol by recrystallizing.

Properties. White powder or crystals, agreeable acid taste, slightly soluble in cold water and alcohol; freely soluble in hot water.

Formation of normal tartrate by action of potassium bicarbonate on this salt is shown in the equation:

$$KHC_4H_4O_6 + KHCO_3 = K_2C_4H_4O_6 + H_2O + CO_2.$$

Potassium Sodium Tartrate, *Rochelle salt,* $KNaC_4H_4O_6.4H_2O$. *Prepared* by neutralizing solution of potassium bitartrate with sodium carbonate, and crystallizing.

Properties. A white powder, or colorless transparent crystals, of cooling, saline taste, soluble in water.

Seidlitz powders contain this salt. They are made by wrapping 120 grains Rochelle salt and 40 grains sodium bicarbonate in a blue paper, and 35 grains tartaric acid in a white paper; to be given in solution while effervescing.

Antimony and Potassium Tartrate, *Tartar emetic,* $[K(SbO)C_4H_4O_6]_2H_2O$. *Prepared* by dissolving freshly precipitated antimonous oxide in solution of potassium bitartrate and crystallizing. The reaction is represented thus:

$$2KHC_4H_4O_6 + Sb_2O_3 = 2K(SbO)C_4H_4O_6 + H_2O.$$

Properties. Colorless, rhombic crystals; nauseous, metallic taste; soluble in water; insoluble in alcohol; poisonous. Antidote, tannic acid.

Iron and Ammonium Tartrate and **Iron and Potassium Tartrate** are made by mixing solution of ferric chloride with tartaric acid and adding ammonia water, or solution of caustic potash, as the case may be. Double compounds are thus

formed, which do not crystallize, but are obtained in the form of scales by evaporating to a syrupy consistency and spreading on glass plates to dry. In this way many of the *scale compounds* of the U. S. P. are obtained. In some cases the metallic hydroxide is precipitated, dissolved in the organic acid and scaled, as described.

Tests for Tartrates.

1. Neutral solutions when heated with calcium chloride give a white precipitate, soluble in caustic potash. Calcium citrate is insoluble.

2. Nitrate of silver gives a white precipitate, which blackens on boiling.

3. Heat chars the acid, giving an odor of burnt sugar.

4. Sulphuric acid chars.

Levo-tartaric acid is like dextro-tartaric acid, except that it turns the plane of polarized light to the left.

Racemic acid forms when equal quantities of dextro- and levo-tartaric acid are mixed in solution. It is optically inactive.

Meso-tartaric acid is an optically inactive tartaric acid, which cannot be decomposed into dextro- and levo-tartaric acid like racemic acid.

Citric Acid, $H_3C_6H_5O_7$, or $C_3H_4(OH)(COOH)_3$. A tribasic tetratomic acid. *Occurs in nature* in the free state in lemons, oranges and other fruits; as calcium citrate in potatoes, beets and wood.

Preparation. By action of calcium carbonate on lemon juice, decomposition of the resulting calcium citrate by sulphuric acid, and crystallizing.

Properties. Clear, colorless, prismatic crystals, containing one molecule water of crystallization; agreeable, acid taste; soluble in water and alcohol, loses water at 135° and melts at 153°.

The citrates commonly used are made by dissolving carbonates in solution of citric acid. Effervescent citrates are dry mixtures of potassium bicarbonate, or other carbonates, and citric acid.

Tests for Citrates.

The official metallic citrates are:

Potassium Citrate, $K_3C_6H_5O_7.H_2O$. Forms colorless crystals, or white, granular powder; soluble in water, of cooling, saline taste.

Lithium Citrate, $Li_3C_6H_5O_7$. Forms a white powder; odorless, with a cooling, faintly-alkaline taste; deliquescent; soluble.

Bismuth Citrate, $BiC_6H_5O_7$. Forms a white, amorphous or faintly crystalline powder; odorless, tasteless, and permanent in air. Made by boiling a solution of citric acid with bismuth nitrate, when it forms as a white powder; insoluble in water, soluble in ammonia water.

Bismuth and Ammonium Citrate, a scale compound. Made by dissolving the bismuth citrate in ammonia water, and evaporating at a low temperature and scaling.

Ferric Citrate. Made by dissolving ferric hydroxide in citric acid, and evaporating to syrup, and pouring in thin layer on slabs to dry in scales.

Citrates of Iron and Ammonium, *Strychnine, Quinine* and *soluble ferric phosphate* are made by mixing ferric citrate with the compounds named, and, in the last case, with sodium phosphate, and scaling.

The *effervescent solution of magnesium citrate,* made by dissolving magnesium carbonate in excess of citric acid, adding syrup, flavoring, and adding about 40 grains of potassium bicarbonate, and quickly sealing in a strong bottle.

1. Neutral solutions boiled with calcium chloride give a white precipitate.

2. Neutral solutions with silver nitrate give a white precipi-

tate, which does not blacken on boiling. Different from tartrates.

3. Alkaline solutions turn green, or reddish-green, with potassium permanganate.

ETHERS AND COMPOUND ETHERS, OR ESTERS.

Chemical Constitution. Ethers are formed by replacement of the hydrogen of the hydroxyl of alcohols by hydrocarbon residues and, therefore, may be said to be oxides of hydrocarbon radicals. The hydrocarbon radicals may be of the same kind, when a simple ether is formed, or they may be of different kinds, forming a mixed or double ether:

$C_2H_5C_2H_5O.$	$C_2H_5CH_3O.$
Simple ether	Mixed or double ether

The ethers may also be considered as the anhydrides of alcohols, thus:

$$2C_2H_5OH = (C_2H_5)_2O + H_2O.$$

Compound Ethers, or Esters, are formed by replacement of the replaceable hydrogen of acids by hydrocarbon residues, and are viewed as salts, thus:

$$(C_2H_5)(C_2H_3O_2).$$
Ethyl acetate

Ethers and compound ethers may be formed from monatomic, diatomic, triatomic or higher alcohols, and from monobasic, dibasic or higher acids; thus giving the possibility of formation of a great number and variety.

General Methods of Preparation. 1. By the action of the bromide or iodide of a hydrocarbon radical upon potassium or sodium alcoholate:

CH_3I	+	CH_3ONa	=	NaI	+	$(CH_3)_2O.$
Methyl iodide		Sodium methylate		Sodium iodide		Methyl ether

2. By the action of sulphuric acid upon alcohols; thus removing water:

$$2C_2H_5OH + H_2SO_4 = (C_2H_5)_2O + H_2SO_4 + H_2O.$$

3. By the action of hydrocarbon chlorides or iodides upon salts:

$$C_2H_5I + KC_2H_3O_2 = KI + C_2H_5C_2H_3O_2.$$

4. By union of alcohols with acids:

$$CH_3OH + HC_2H_3O_2 = CH_3C_2H_3O_2 + H_2O.$$

Occurrence in Nature. In plants and animals in the form of fats and fatty oils; in plants, as essential oils; in spermaceti and wax.

General Properties. Lower members, usually volatile liquids, of peculiar aromatic, agreeable odor. They become less volatile and less fluid as they advance in the series, until they finally become solid non-volatile bodies. They are neutral and the compound ethers are saponifiable by the action of alkalies.

Methyl Ether $(CH_3)_2O$. Made by action of sulphuric acid on methyl alcohol.

Properties. A gas at ordinary temperature. Liquefied by pressure to a mobile, colorless, inflammable liquid.

Ethyl Ether, Ether $(C_2H_5)_2O$. (*Sulphuric ether.*) *Preparation.* By heating in a retort to 140°, ethyl alcohol and sulphuric acid, having the apparatus so arranged that more alcohol may be added from time to time, and condensing the vapors in a cooled receiver. The distillate is then mixed with calcium oxide and chloride and redistilled. The chemical changes are represented in the equations:

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Ethyl-sulphuric acid}}{C_2H_5HSO_4} + \underset{\text{Water}}{H_2O},$$

$$\underset{\text{Ethyl-sulphuric acid}}{C_2H_5HSO_4} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} = \underset{\text{Ethyl ether}}{(C_2H_5)_2O} + \underset{\text{Sulphuric acid}}{H_2SO_4}.$$

The power of sulphuric acid to convert an unlimited amount of alcohol into ether, as this equation would indicate, is not

strictly true, because of the side reactions; some of the acid being deoxidized by carbonization of impurities in alcohol, and some being rendered inert by dilution with water, etc.

Properties. A clear, colorless, mobile, volatile, *inflammable* liquid; soluble in ten parts of water, in alcohol, chloroform, benzene and oils; specific gravity about 0.716, boiling point 35.5°. It causes intoxication and insensibility when inhaled, and the vapor is given by inhalation, without air, because of the oxygen it contains. Official ether contains 96 per cent. ether, 4 per cent. alcohol. The anhydrous ether is obtained by distilling from metallic sodium. Ether vapor forms an explosive mixture with air. Ether dissolves oils, fats, resins, bromine, iodine, phosphorus and many salts.

Spirit of ether is a mixture of one part ether and two parts alcohol. *Compound spirit of ether,* or *Hoffmann's anodyne* contains, in addition to the above, ethereal oils.

Methyl-Ethyl Ether, $CH_3C_2H_5O$. Made by action of ethyl iodide on sodium methylate, thus:

$$C_2H_5I + NaOCH_3 = NaI + C_2H_5OCH_3.$$

Properties. Colorless, volatile, inflammable liquid; boils at 11°. *Used* as anæsthetic.

Acetic Ether, Ethyl Acetate, $(C_2H_5)(C_2H_3O_2)$. *Made* by distilling a mixture of sodium acetate, ethyl alcohol and sulphuric acid, shaking the distillate with calcium chloride and redistilling. The reaction is represented thus:

$$C_2H_5OH + NaC_2H_3O_2 + H_2SO_4 = C_2H_5C_2H_3O_2 + NaHSO_4 + H_2O.$$

Properties. Clear, colorless, volatile liquid; aromatic odor, pungent taste; soluble in chloroform, alcohol, ether and 17 parts water.

Ethyl Nitrite, Nitrous ether, $C_2H_5NO_2$. *Made* by distilling a mixture of ethyl alcohol, sodium nitrite and sulphuric acid; washing with cold water and sodium carbonate, to remove

alcohol and neutralize acid; and mixing with dried potassium carbonate, to remove water.

Properties. Mobile liquid, agreeable odor, sweet taste, boils at 86°. Used in making *sweet spirit of nitre,* by dissolving four parts in 96 parts alcohol.

Glyceryl Trinitrate, Nitroglycerine, $C_3H_5(NO_3)_3$. Made by the action of a mixture of nitric and sulphuric acids on glycerine in the cold.

Properties. A clear, colorless, or slightly yellowish, oily liquid; soluble in alcohol and ether, insoluble in water; sweetish, burning taste; poisonous; solidifies at —20°; burns when heated in an open vessel, but explodes if the heat exceed 250°, or by concussion. *Dynamite* is nitroglycerine mixed with infusorial earth. *Spirit of glonoin* is a one per cent. alcoholic solution of nitroglycerine.

Amyl Nitrite, $C_5H_{11}NO_2$. Made like ethyl nitrite.

Properties. A clear, pale-yellow liquid; aromatic, apple-like odor; burning taste; specific gravity 0.872, boiling point at 96°.

Nitrite of amyl is used in medicine to lessen arterial tension and stimulate the heart's action, it is administered by inhalation.

The Natural Fats.

The natural fats, or true fats, are compound ethers formed by the union of the radical of the triatomic alcohol glycerine, $C_3H_5(OH)_3$, with fatty acids; chiefly oleic, palmitic and stearic acids. The salts formed by this union are known as *olein,* $C_3H_5.(C_{18}H_{33}O_2)_3$; *palmitin,* $C_3H_5.(C_{16}H_{31}O_2)_3$; and *stearin,* $C_3H_5.(C_{18}H_{35}O_2)_3$. Of these three compounds, olein is a liquid at the ordinary temperature, while palmitin and stearin are solids; and the fat is liquid or solid, according to the proportionate quantities of these constituents.

The fat oils are distinguished from the essential oils by the permanent stain which fats produce upon paper, and by their non-volatility.

Occurrence in Nature and Properties of Fats. The fats are found in minute quantity in all parts of plants, and in all parts of animal tissues except normal urine. They occur in abundance in the seeds of many plants, and under the skin and around the intestines of animals.

When pure, they are colorless, odorless, and tasteless, though taste, color and odor are often imparted by foreign substances or products of decomposition. The decomposition of fats is known as rancidity; in which the fatty acid is liberated. All fats are lighter than water, and the solid ones fuse below the boiling point of water (100°); they cannot be distilled at the atmospheric pressure without decomposition. When fats are heated, some of the decomposition products formed have an exceedingly disagreeable odor, as is shown in the case of acrolein, an aldehyde formed from glycerine by dehydration.

Some of the fats absorb oxygen of the air and generate sufficient heat to set fire spontaneously to cotton or wool saturated with them. These fats become thick and finally form solid shining masses. On account of these properties they are largely used in painting, and are called *drying oils.* Examples of drying oils are croton oil, linseed oil, hemp oil, castor oil and cod-liver oil. Their drying properties are due to the presence of linoleic acid instead of oleic acid. The presence of albuminous impurities, which prevent the hardening of drying oils, may be removed by shaking with sulphuric acid.

Non-drying oils of importance are almond oil, palm oil, cocoanut oil, olive oil and cotton-seed oil.

Waxes, while they are not glycerides like ordinary solid and liquid fats, are compound ethers showing great resemblance to fats. The *liquid waxes* are esters of monatomic alcohols, and include dolphin oil and sperm oil. *The solid waxes* are esters of the higher monatomic alcohols, with higher fatty acids in the free state. They include beeswax, Chinese wax and spermaceti.

Decomposition of Fats is brought about in various ways, depending upon the products it is desired to form:

1. By the action of metallic oxides in the presence of water, whereby a salt of the metal with the organic acid is formed and glycerine is set free. This method is employed in making *lead plaster,* which consists in boiling olive oil with lead oxide (litharge) and water, until a homogeneous mass results. Lead plaster is chiefly oleate of lead, which is completely insoluble in water, but soluble in benzene and chloroform. This equation represents its formation:

$$\underset{\text{Olein}}{2C_3H_5(C_{18}H_{33}O_2)_3} + 3PbO + \underset{\text{Water}}{3H_2O} = \underset{\text{Glycerine}}{2C_3H_5(OH)_3} + \underset{\text{Lead oleate}}{3Pb(C_{18}H_{33}O_2)_2}.$$

2. By the action of steam or water, under pressure, resulting in the separation of glycerine and the fatty acid, thus:

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3H_2O = C_3H_5(OH)_3 + 3H.C_{18}H_{35}O_2.$$

3. By action of alkaline hydroxides, resulting in formation of a salt of the alkali with the fatty acid, or soap, and liberation of glycerine. Soft soap is formed from potassium; hard soap, from sodium. The reaction is represented in the equation:

$$\underset{\text{Olein}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\substack{\text{Sodium}\\\text{hydroxide}}}{3NaOH} = \underset{\text{Soap}}{3NaC_{18}H_{33}O_2} + \underset{\text{Glycerine}}{C_3H_5(OH)_3}.$$

Green soap, soft soap, is made from linseed oil by action of caustic potash. It is a yellowish-brown soft-solid, soluble in water and alcohol, used for medical and surgical purposes.

Liniment of ammonia is made by mixing ammonia water and cotton-seed oil, with 5 per cent. of alcohol. It contains ammonia soap.

Liniment of lime, carron oil, made by shaking up a mixture of equal parts of lime water and linseed oil or olive oil. It contains calcium soap.

CARBOHYDRATES, OR SACCHARIDS.

This group of organic bodies embraces a number of important compounds widely distributed in the vegetable kingdom, and largely used as food in the support of animal life.

As originally defined, these compounds were said to contain six atoms of carbon, or some multiple of six, in the molecule, and hydrogen and oxygen in the proportions to form water. While this statement is true in reference to most of these bodies, it cannot be taken as a definition; for carbohydrates have been made whose molecules contain carbon in quantities which have no relation to six, and others are known in which hydrogen and oxygen are not combined in the proportions to form water. While the term carbohydrate is no longer restricted to the bodies which it formerly included, the name is still retained in its broadened sense.

The carbohydrates are aldehydes and ketones of the hexatomic alcohols, in some cases, and in others, they are the anhydrides of these aldehydes. The hexatomic alcohol $C_6H_8(OH)_6$ is derived from the hydrocarbon hexane by replacement of six hydrogen atoms by 6OH. By gentle oxidation of this alcohol hydrogen is removed, and it is converted into the corresponding aldehyde, $C_6H_{12}O_6$, mannose, a sugar, having the formula of a number of the carbohydrates, all of which behave like aldehydes.

A second group of the carbohydrates, having the formula $C_{12}H_{22}O_{11}$, are probably anhydrides of the group $C_6H_{12}O_6$. Thus: $2C_6H_{12}O_6 - H_2O = C_{12}H_{22}O_{11}$.

A third group of the carbohydrates, having the formula $C_6H_{10}O_5$, are still more complex anhydrides of the first. Thus: $(C_6H_{12}O_6) - H_2O = (C_6H_{10}O_5)_{nn}$.

These anhydrides, by processes of hydrolysis, may be made to take up water, and thus revert to the other forms. The aldehydic nature of the carbohydrates is shown in the case of

glucose which, by further oxidation, is converted into an acid, and, by action of nascent hydrogen, is reconverted into the alcohol, mannitol; a behavior similar to that which we have seen in other aldehydes.

The bodies studied in this group are *sugars, starches, gums* and a number of compounds obtained by artificial means. The termination, *ose,* is generally used in naming these bodies to indicate that they belong to the same natural group.

Occurrence in Nature. Carbohydrates are found in great abundance in the vegetable kingdom as starch, sugar and cellulose. In the animal kingdom they are found also, as represented by milk-sugar and bees' honey.

General Properties. Most of the carbohydrates, when pure, are white solid substances, usually soluble in water. Some of them have a more or less sweet taste. They are not volatile, and easily undergo decomposition by the action of heat. The carbohydrates are either fermentable, or can usually be converted into fermentable substances. They are neutral in reaction, and behave like aldehydes—being converted into acids by oxidation, and, in some cases, forming alcohols by action of nascent hydrogen. Many of them are active reducing agents, deoxydizing alkaline solutions of salts of copper, mercury and bismuth.

Classification of Carbohydrates. They were formerly classified into three groups, according to composition, thus:

Glucoses.	Saccharoses.	Amyloses.
$C_6H_{12}O_6$.	$C_{12}H_{22}O_{11}$.	$C_6H_{10}O_5$.
Grape-sugar.	Cane-sugar.	Starch.
Fruit-sugar.	Melitose.	Dextrin.
Mannitose.	Maltose.	Gums.
Inosite.	Milk-sugar.	Cellulose.
		Glycogen.

The above system of classification is not sufficiently comprehensive to include all the carbohydrates at present known, so they have been rearranged in the three following groups:

Mono-saccharids are carbohydrates which, by digestion with dilute acids, do not yield any other forms of sugar. They are, therefore, the simplest of the sugars, and include the members of the class formerly referred to as glucoses. They contain from three to nine carbon atoms in the molecule, an equal number of oxygen atoms, and twice as many atoms of hydrogen. These sugars are named according to the number of carbon atoms they contain, thus:

Trioses, three carbon atoms; Tetroses, four carbon atoms; Pentoses, five carbon atoms; Hexoses, six carbon atoms; Heptoses, seven carbon atoms; Octoses, eight carbon atoms; Nonoses, nine carbon atoms.

The group of hexoses embraces the best-known members of this class; the others are chiefly of scientific interest.

The Di-saccharids are carbohydrates which split up into two different sugars, when boiled with dilute acid. These include the sugars found in the group of saccharoses of the old classification: *Pentabioses,* $C_{10}H_{18}O_9$; *Hexabioses,* $C_{12}H_{22}O_{11}$; *Hexatrioses,* $C_{18}H_{32}O_{16}$.

The Poly-saccharids comprise carbohydrates of vegetable origin whose molecular formulæ have not been determined; they split into more than two different sugars when boiled with dilute acid. Some are crystallizable as gentianose, of gentian root, and lactosan of soap bark. Others are non-crystallizable and represented by starches, dextrins and celluloses, corresponding to the amyloses of the old classification:

1. Monosaccharids.

Properties. Neutral, colorless, odorless, and sweet-tasting bodies, easily soluble in water, insoluble in ether, slightly soluble in alcohol.

They are aldehydes and ketones and are easily oxidized and, therefore, reduce certain metallic salts, such as copper.

The trioses, hexoses and nonoses readily undergo alcoholic fermentation; the pentoses, heptoses and octoses do not. Of the monosaccharids the hexoses are of practical interest.

The Hexoses, or Glucoses, are divided into two groups: *The aldehyde, or aldose group; and the ketone, or ketose group.*

The members of the aldehyde group of interest are:

Dextrose, Glucose, or Grape-sugar, $C_6H_{12}O_6$. *Found* widely distributed in the vegetable kingdom, in grapes, in most sweet fruits, in sprouting grains, and in honey; generally occurs with an equal amount of levulose. Occurs in minute quantity in blood and, in large amount, in diabetic urine.

Formed in plants by action of vegetable acids on starch. Artificial preparation by boiling starch, or cellulose, with dilute mineral acid, forming first dextrin and then dextrose, neutralizing the acid with lime, and drawing off the clear liquid and evaporating.

Properties. Generally seen as a syrup, or thick liquid, but may be obtained crystalline. Soluble in own weight of water, slightly soluble in alcohol, less sweet than cane sugar. It first loses water when heated and is converted into glucosan $C_6H_{10}O_5$, and then forms caramel. Dextro-rotary; a strong reducing agent; combines with various oxides and other bodies to form glucosides.

Mannose, $C_6H_{12}O_6$, is obtained by careful oxidation of mannite, $C_6H_8(OH)_6$. It is a hard, friable powder; resembles grape sugar.

Galactose, $C_6H_{12}O_6$ (*Cerebrose*). Formed with dextrose when milk-sugar, gums and mucilages are boiled with dilute H_2SO_4. Formed by decomposition of the glucoside, cerebrin, which is found in the brain. May be separated from dextrose by its solubility in absolute alcohol. Crystalline solid, reduces copper solution and ferments with yeast.

Members of the *Ketone* group of hexoses are:

Levulose, $C_6H_{12}O_6$ (*Fructose*), *Fruit-sugar.* Occurs mixed with glucose in sweet fruits and honey. *Made* by heating cane-sugar with dilute acids, which forms dextrose and levulose. Separated from former by mixing with slacked lime and water, when levulose forms an insoluble compound with calcium, which is separated and decomposed with CO_2.

Properties like glucose, but may be crystallized from alcohol; sweeter, levo-rotary. Easily assimilated; does not increase sugar in urine of diabetics, and used for them as "*diabetin.*"

Inosite (*muscle-sugar*), $C_6H_{12}O_6$. *Occurs* in muscles, lungs, liver, kidney, spleen, brain. In vegetable kingdom, in unripe beans.

Properties. Only resemblance to sugars is sweet taste. Now thought to be a derivative of benzene, and not a sugar. Large, efflorescent, rhombic tables, or lumps of fine crystals; soluble in water and dilute alcohol.

2. Disaccharids, or Saccharoses.

An important class. All capable of hydrolysis by dilute acids and certain ferments, yielding monosaccharids. This process is called inversion. Cane sugar does not reduce Fehling's solution; the other members do.

Cane-sugar, Saccharose, Saccharum, Sucrose, *Beet-sugar,* $C_{12}H_{22}O_{11}$.

Occurrence in Nature. In juices of many plants, in fruits, in juice of sugar cane (Saccharum officinarum), sorghum (Sorgo saccharatum), beet root, maple and several species of palm. Found in plants containing no free acid.

Prepared by expressing the juices of cane sugar, heating and adding milk of lime, to precipitate vegetable albuminous matter and phosphates. The clear liquid is then evaporated, filtered through bone charcoal, and concentrated in vacuum

pans to crystallize. The residue of " mother liquor " is used as syrup.

Properties. When allowed to crystallize slowly, it forms large, prismatic, transparent crystals, called " rock candy." It also forms hard, white, granular crystals. Sugar is soluble in .5 parts cold water, and in all proportions of hot water, and in 175 parts of alcohol. It fuses at 160°, and forms an amorphous transparent mass known as "barley sugar "; at higher temperatures it turns brown, forming caramel, and finally oxidizes by further heating.

Cane-sugar is a strong reducing agent; this property can be shown by mixing it with chlorate of potash and sulphuric acid, when violent deflagration takes place. An acid solution of potassium permanganate is decolorized by a solution of cane-sugar for the same reason.

Cane-sugar does not reduce alkaline copper solution; it is not directly fermentable, but can be converted into fermentable forms; it produces compounds with many other bodies, and these compounds are called *Sucrates.*

Lactose, Milk-sugar, Saccharum Lactis, $C_{12}H_{22}O_{11}.H_2O$. This sugar is found in the milk of mammals. It is made by evaporating the whey of cow's milk. Cow's milk contains from four to five per cent. of milk-sugar; human milk contains from six to seven per cent.

Properties. Milk-sugar occurs in hard, white, prismatic crystals or masses; it is soluble in six parts of cold water, or one part of boiling water.

This sugar is not so sweet as cane sugar; it does not ferment readily with yeast, but ferments to lactic or butyric acid by the action of these ferments; it reduces alkaline copper solution.

Maltose, Malt-sugar, $C_{12}H_{22}O_{11}$. In the germination of grain, malt-diastase is formed, and this ferment, acting upon starch present in the grain, produces malt-sugar. Extracts of

malt are used in medicine for the purpose of aiding the digestion of starchy foods; the diastase of these extracts converting the starch into malt-sugar, a soluble form of carbohydrate.

Malt-sugar is also formed by the action of saliva or of dilute sulphuric acid on starch; the continued action of sulphuric acid on starch results in the formation of dextrose.

Maltose is soluble in water or alcohol; it crystallizes in fine needles; it ferments with yeast to form alcohol; it reduces alkaline copper solution.

Melitose is a sugar obtained from Australian manna.

3. The Polysaccharids.

To this group belong a great number of carbohydrates of high molecular weight, generally insoluble, not diffusible, and capable of splitting into more than two sugars by the action of dilute acids and ferments. When boiled with acids they generally change into dextrin, di-saccharids, and finally, monosaccharids. The exact molecular weight is not known, but by reference to Raoult's method the probable molecular weight of dextrine is $(C_6H_{10}O_5)_{12}$, and of soluble starch, $(C_6H_{10}O_5)_{30}$.

The subdivisions of this group embrace the *starch group*, the *cellulose group*, and the *gum group*.

(*a*) The Starch Group.

Starch, Amylum, $(C_6H_{10}O_5)_x$. Starch is found in nearly all plants, in the seeds, roots and stems; it occurs most abundantly in the cereals, rice, potatoes, and the seeds of plants. Microscopic starch granules are imbedded in the cells of the plant, in much the same way as fat granules occur in the animal body.

Starch granules are somewhat oval in shape, having an eccentric nucleus around which are placed concentric layers of substance, resembling the appearance of an oyster-shell. In potato-starch the granules are large and oval, in corn-starch the gran-

ules are less oval and much smaller. The source from which starch is obtained may be determined by means of the microscope, on account of differences in appearance of the granules.

The preparation of starch is a mechanical process, which consists in first comminuting or grinding the vegetable substance, and then washing with water. In this way the starch granules are removed, and the water may be separated by decantation.

Properties. White, amorphous, odorless, tasteless, friable masses; insoluble in cold water, alcohol or ether. When starch is boiled with water, the granules swell, and finally burst, forming a thick mucilaginous liquid, known as starch paste; by long boiling it is converted into soluble dextrine. The conversion into dextrine is also produced by dry heat at 175°, or by boiling with dilute sulphuric acid.

The characteristic test for starch is iodine. This test is applied by mixing an aqueous solution of iodine with cold mucilage of starch, when a deep blue color is produced.

Glycogen, $(C_6H_{10}O_5)_n$. Glycogen occurs in the liver of animals, in the yolk of egg, the embryo and in some mollusks.

Glycogen resembles dextrine; it dissolves in water, but is insoluble in alcohol or ether; it is dextro-rotary. Glycogen of the liver is changed to maltose and dextrose by a liver ferment or the liver cells. Iodine gives a reddish-brown color with glycogen which disappears on heating and returns when cooled.

Glycogen may be prepared for experiment as follows:

Preparation. Use a liver taken from an animal just killed, or oysters just removed from the shell. Cut one half rapidly into small pieces and place it into four times its weight of boiling water which has been slightly acidified with acetic acid. Lay the other half aside, keeping it moist for twenty-four hours, for subsequent examination. See page 313.

After boiling the first portion for a few minutes, remove the pieces, grind in a mortar with clean sand, return to the water,

and continue boiling for several minutes; filter while hot. The liquid thus obtained has an opalescent appearance, and contains glycogen in solution.

The solution of glycogen may be purified as follows: Add, alternately, a few drops of hydrochloric acid and potassium mercuric chloride, as long as a precipitate of proteids forms. This may be determined more accurately by testing a small portion of the liquid separately from time to time. When the precipitation is complete, filter, and add to the filtrate, double its volume of alcohol; the glycogen will precipitate as a white powder. Filter, and wash the precipitate with a mixture of one part water and two parts alcohol. Dissolve the residue in water.

(*b*) The Cellulose Group.

Cellulose, Lignine, Plant Fibre, $(C_6H_{10}O_5)_3$. Occurs in nature as plant skeleton; also as cotton, hemp and flax. Absorbent cotton is pure cellulose.

Properties. White, translucent, insoluble: soluble in ammoniacal solution of basic cupric carbonate.

Cellulose does not give a blue color with iodine. When mixed with sulphuric acid it swells, dissolves, and is precipitated from solution by adding to water; this precipitate is called *amyloid.* Amyloid, as its name implies, is closely related to starch, and gives a blue color with iodine.

Cellulose is converted into dextrine and dextrose by boiling with diluted sulphuric acid.

Parchment paper is made from cellulose by dipping paper into a solution made by mixing two volumes of sulphuric acid and one volume of water.

Trinitro cellulose, $C_6H_7O_2(NO_3)_3$, is explosive gun-cotton. Made by steeping cotton in a mixture of one part strong nitric, and three parts strong sulphuric acid, for a few minutes; re-

moving, squeezing dry, and placing in fresh acid forty-eight hours; removing, pressing dry, washing with water, and then weak sodium carbonate solution. The cotton retains its appearance, but is very explosive.

Tetranitro cellulose, or *pyroxylin,* is used for making collodion by dissolving in a mixture of ether and alcohol. Guncotton is used in making smokeless powder. Formation of the different compounds dependent upon length of time cotton is acted on by the acids.

(*c*) The Gum Group.

These are amorphous, of vegetable origin, soluble in water or swelling in it like tragacanth, insoluble in alcohol, converted into glucose by boiling with dilute sulphuric acid.

Dextrine or British Gum $(C_6H_{10}O_5)_n$. *Preparation.* By action of dilute acid on starch, or dry heat to 175°, or action of diastase on starch.

Properties. Colorless, or yellowish, amorphous powder; resembles gum arabic; soluble; reduces copper solution; colored wine-red by iodine.

Acacia, Gum Arabic. Exudation from *Acaciæ Senegal.* In composition it is said to be the calcium salt of arabic acid.

Properties. Soluble in two parts water; solution has acid reaction with litmus, and precipitates with lead acetate or ferric chloride. Gums from cherry, peach, flaxseed, &c., are members of this group.

Practical Note.—In the treatment of certain diseases, such as diabetes mellitus, it becomes necessary to exclude carbohydrate food from the diet, as far as possible. Articles of food containing a minimum quantity of carbohydrate are as follows: Meats of all kinds, fresh or salted; soups made from meat without flour; game, poultry, oysters, fish, lobsters, crabs, eggs, butter, new cheese, oils and fats. All vegetable substances contain carbohydrate in the form of cellulose, or plant fibre, but in a case of diabetes, the green vegetables are allowed, as they do not

contain starch or sugar to any great extent. The green vegetables referred to are cabbage, Brussels sprouts, spinach, endive, the green leaves of lettuce, cauliflower, broccoli, string beans, tomato, water cresses, celery tops, asparagus tops, turnip tops, young onions, cucumber, pickles and olives. Of fruits, and other articles permitted in a carbohydrate-free diet, are apples, lemons, strawberries, almonds, walnuts, butter-nuts, pecans, filberts, Brazil nuts, but not chestnuts. To these may be added unsweetened jellies, cream, milk, buttermilk, unsweetened tea or coffee; claret, Burgundy, still Moselle, and sherry wines; brandy, whiskey, gin and carbonated waters.

Tests for Carbohydrates.

1. MONO-SACCHARIDS.

Glucose. Employ a three per cent. aqueous solution.

1. *Trommer's Test.* To about 5 cc. of solution in a test-tube add an equal volume of strong solution of caustic soda or caustic potash solution, and then a dilute solution of cupric sulphate, drop by drop, as long as the precipitate formed continues to redissolve, forming a clear blue liquid. Heat the mixture, and note the reddish-yellow precipitate of cuprous oxide. Apply the same test to normal urine and to diabetic urine.

2. *Fehling's Test.* Fehling's solution is made as follows: Dissolve 34.64 gm. of pure crystallized cupric sulphate in water to make 500 cc. Dissolve 173 gm. pure crystallized sodium potassium tartrate, and 60 gm. sodium hydroxide, each in 200 cc. of water and make up to 500 cc. with distilled water. When the solution is to be used, mix equal quantities of the copper sulphate and sodium tartrate solutions. Ten cc. of the mixed solutions will be reduced by .05 gm. of glucose.

Boil a few cc. of the Fehling's solution in a test-tube (it should remain clear) and then add a few drops of the glucose solution and allow to stand a few minutes. Notice the precipitate of reddish-yellow cuprous oxide. Apply the above test to normal and diabetic urine.

Note.—A flocculent, yellowish precipitate is sometimes produced, when Fehling's solution is heated with urine, by an excess of urates or earthy phosphates, which must not be mistaken for glucose.

3. *Boettger's Test.* To some of the glucose solution add an equal volume of strong sodium carbonate solution (1 in 3), and then a little bismuth subnitrate: shake and boil. The subnitrate assumes a grayish or black color, depending on the amount of glucose present. Albumen and substances containing sulphur interfere with this test.

4. *Fermentation Test.* Fill a test-tube with the glucose solution, add some yeast and invert over a dish containing the same solution. Allow the test-tube to stand for twenty-four hours, and test the evolved gas (CO_2) with lime-water.

2. DI-SACCHARIDS.

(*a*) **Cane-sugar.** Use a 2 per cent. aqueous solution.

1. Apply tests 2 and 3, and note the negative results.

2. To some of the solution in a test-tube add a few drops of dilute sulphuric acid; boil for several minutes, allow to cool, neutralize with caustic soda and re-apply tests 2 and 3. Observe that the sugar has undergone inversion by action of the acid, being converted into dextrose and levulose.

(*b*) **Maltose.** Use a 2 per cent. aqueous solution.

Apply tests 2 and 4, comparing with glucose.

3. POLY-SACCHARIDS.

(*a*) **Starch.** 1. *Examine under the microscope* and note the characteristic granules. Examine the granules of potato, corn, wheat and rice starch, noting the differences in appearance.

2. *Solubility.* Test by adding water to powdered starch, filter, and test the filtrate by adding a drop of iodine solution. Notice that no reaction is obtained.

3. *Starch Paste.* Take a small quantity of starch and rub with a little water, then pour the mixture into about 25 cc. of boiling water, allow the liquid to cool and notice that it acquires a mucilaginous appearance and consistency. Add iodine solution and note blue color.

4. Add a few drops of solution of tannic acid to the starch solution; a yellowish precipitate is formed, soluble upon application of heat.

5. Test the starch solution with Fehling's solution and note the negative result.

6. Boil 25 cc. of the starch solution with a few drops of dilute sulphuric acid for ten minutes and note the change in appearance. Neutralize a portion of this solution with caustic soda and test with Fehling's solution. Note reaction for glucose.

7. To about fifteen cc. of the starch solution add a few cc. of saliva and heat in the water-bath at about 40° C. for fifteen minutes. Test the resulting solution with Fehling's solution and note the reduction, indicating maltose.

(*b*) **Dextrine.** 1. Employ a 2 per cent. aqueous solution of pure dextrine and apply the tests given under starch, noting the results.

2. Add a few drops of the dextrine solution to some alcohol in a test-tube and note the precipitate which is redissolved by adding water.

3. Add basic lead acetate solution to the solution of dextrine and note the result.

(*c*) **Glycogen.** The glycogen solution obtained as directed on page 308, may be tested as follows:

1. Add a drop of iodine solution to a portion of the glycogen solution in a test-tube, and note the dark-red color. This color disappears on heating and returns when the liquid cools. Compare with dextrine.

2. Test with Fehling's solution and note the negative result.

3. Boil with a few drops of dilute sulphuric acid, neutralize with sodium hydroxide, and apply Fehling's solution; note reaction for glucose.

4. Add basic lead acetate solution and compare with dextrine.

5. Add saliva to some of the glycogen solution and heat for fifteen minutes on the water-bath at 40° C. Divide into two portions: test one half with iodine solution for glycogen, and the other half with Fehling's solution for sugar.

Make an extract of the half of the liver or oysters that has been reserved. See page 308. Test for glycogen with iodine solution, and for reducing sugar with Fehling's solution.

GLUCOSIDES.

Glucosides are compounds which decompose by the action of dilute acids, forming glucose or a related carbohydrate. The decomposition of a glucoside appears to be a process of hydration, and it is effected not only by the action of dilute acids but by boiling with weak alkalies, and by the action of ferments. The glucosides are usually obtained from the vegetable kingdom.

The chemical behavior of glucosides indicates that their structure corresponds to the molecule of a compound ether, in which glucose takes the part of the basic radical.

Glucosides are prepared from the plant in which they occur by extracting with water or alcohol, decolorizing with animal charcoal, and crystallizing by evaporation. They can be made artificially by dissolving glucose in different alcohols, and passing gaseous hydrochloric acid through the solution.

The glucosides are usually neutral, soluble in water and capable of being crystallized. Some of them, such as solanin, contain nitrogen and resemble the alkaloids; others, such as myronic acid, have a slightly acid character. Many of them are optically active, but the direction of their rotation shows no relation to the sugar formed by their decomposition. Some of the glucosides represent the active principles of plants and are employed in medicine, like alkaloids. The termination, *in*, is generally employed in naming the members of this class.

The names and source of some of the more important glucosides are as follows:

Adonin, obtained from Adonis vernalis, and sometimes used as a cardiac tonic.

Amygdalin, $C_{20}H_{27}NO_{11}$, is found in the bitter almond and cherry-laurel. Amygdalin decomposes by action of the ferment, *emulsine,* in presence of water, forming glucose, benzoic aldehyde, and hydrocyanic acid. It is a white, crystalline powder.

Arbutin is a bitter substance found in Uva ursi.

Cathartic acid is found in senna.

Colocynthin is a purgative principle found in colocynth-fruit.

Digitalin is obtained from *Digitalis purpurea,* and it consists of a mixture of glucosides, viz.: *Digitonin,* $C_{31}H_{52}O_{17}$, a yellowish, amorphous body; soluble in diluted alcohol. *Digitalin,* $C_5H_8O_2$, a crystalline, bitter solid; soluble in alcohol; insoluble in water. *Digitalein,* a white, amorphous, bitter solid; soluble in water or alcohol. *Digitoxin,* $C_{21}H_{32}O_7$, a colorless, crystalline solid; slightly soluble in alcohol; insoluble in water. Digitoxin is not a glucoside.

Myronic acid, $C_{10}H_{19}NS_2O_{10}$, found as potassium salt in black mustard-seed oil. This salt is called *sinagrin;* it is decomposed by action of the ferment, myrosin, into dextrose, allyl mustard oil and potassium bisulphate.

Allyl mustard oil, C_3H_5NCS, is the sulphocyanide of the radical, C_3H_5, from propylene, C_3H_6, isomeric with glyceryl. Glyceryl may be converted into allyl alcohol, C_3H_5OH, and artificial mustard oil can be made from this. Mustard oil is a pale-yellow liquid, acrid odor and burning taste. Allyl sulphide, $(C_3H_5)_2S$, is found in garlic.

Phloridzin is obtained from bark of the root of apple, cherry and pear; its introduction into the circulation causes glycosuria.

Salicin, $C_{13}H_{18}O_7$, is found in the willow. It decomposes into glucose and *salicylic alcohol,* ($C_6H_4OHCH_2OH$). Salicylic

alcohol may be oxidized into salicylic acid. Salicin occurs in white, silky, needle-shaped crystals; soluble in water; bitter taste.

Strophanthin is found in the seeds of strophanthus. It is used as a heart tonic.

Solanin, a poisonous body found in potato-sprouts and in other solanaceous plants.

NITROGENOUS BODIES OF SIMPLE STRUCTURE.

The nitrogen of organic bodies is contributed from three sources, viz., ammonia, cyanogen and nitric acid, or derivatives of these compounds. In many of the complex nitrogenous bodies of the aromatic series, and in the nitrogenous bodies of the proteids, nitrogen is contained in the ammonia forms.

In the present chapter, only those nitrogenous bodies having a simple structure will be considered.

The ammonia forms of nitrogen embrace the amines, amides and amido-acids and their derivatives. These are found in the various organic bases, generally known as alkaloids, and occurring as the product of animal or plant life.

The cyanogen forms of nitrogen contain the compound radical cyanogen, CN, and constitute the group of bodies known as cyanogen and cyanides.

The nitric acid forms comprise the organic nitrates, nitrites, and nitro-compounds. Nitro-compounds contain the radical NO_2; they differ from nitrites in the fact that this radical replaces hydrogen in forming nitro-compounds, while the NO_2 group, in nitrites, is united to a basic radical, producing a compound ether.

The nitric acid derivatives are not found in nature, but are made by artificial means, and they often constitute highly explosive substances, such as nitro-glycerine, trinitro-cellulose, &c.

AMINES AND AMIDES.

Amines are bodies formed by replacement of hydrogen in ammonia by alcohol radicals, thus:

$NH_2(CH_3)$ Methyl amine $\qquad$ $NH_2(C_2H_5)$. Ethyl amine

Primary amines are formed when one hydrogen atom is replaced by the radical; *secondary* and *tertiary amines* are formed when two and three hydrogen atoms are so replaced.

Ammonium bases are formed when all the hydrogen of the ammonium radical has been replaced by an alcohol radical, thus:

$N(CH_3)_4OH$, Tetra-methyl ammonium hydroxide.

Amines are further subdivided into *mon-amines, di-amines, tri-amines,* &c., according as *one, two, three* or more molecules of ammonia are represented, thus:

$(NH_2)_2C_2H_4$, Ethylene diamine.

The properties of amines are much like those of ammonia; they are usually soluble, have an ammoniacal disagreeable odor, and are strongly basic; they combine with acids with retention of hydrogen; their chlorides form double compounds and precipitates with perchloride of platinum. The amines formed from methane are gaseous, those formed from ethane are liquids.

The resemblance of amines to ammonia is well shown in the following equation, which represents the reaction taking place between trimethylamine and hydrochloric acid, forming trimethyl-amine hydrochloride, thus:

$$N(CH_3)_3 + HCl = N(CH_3)_3HCl.$$

Notice that this base unites with the acid with retention of the hydrogen, to form a salt.

Amides are derived from ammonia by replacement of its hydrogen atoms by acid radicals, thus:

$NH_2(C_2H_3O)$, Acetamide.

The naming of amides follows the same rules that apply to amines.

In properties, the amides resemble ammonia like amines, but they are less basic than the latter, on account of the presence of the acid radical.

Formamide, NH_2CHO. Made by heating alcoholic solution of ammonia with ethyl formate. Also made by dry distillation of ammonium formate, thus:

$$\underset{\text{Ammonium formate}}{NH_4HCO_2} = \underset{\text{Formamide}}{NH_2HCO} + \underset{\text{Water}}{H_2O}.$$

Properties. A colorless liquid, soluble in water or alcohol.

Formamide combines with chloral to produce chloral-formamide, or chloralamide, having the formula, $NH_2CHO.C_2HCl_3O$.

Chloralamide is a colorless, slightly bitter, crystalline solid; soluble in twenty parts of water. Hot water decomposes this compound into chloral hydrate and ammonium formate; it is also decomposed by alkalies, but not by acids. Used as an hypnotic in ten to forty grain doses.

Amido-acids. The radical NH_2 is known as amidogen. When amidogen replaces the hydrogen of an acid radical, the resulting compound is an amido-acid, thus:

$H.C_2H_2(NH_2)O_2$, Amido-acetic acid.

These compounds show both acid and basic properties, and many of them are formed during life in animal tissues.

Amido-formic Acid, Carbamic acid, $H.NH_2CO_2$. This acid is found in commercial ammonium carbonate, as ammonium amido-formate, having the formula, $NH_4NH_2CO_2$. The ammonium salt is produced by the action of carbon dioxide on ammonia, as shown in the following equation:

$$CO_2 + 2NH_3 = NH_4NH_2CO_2.$$

Amido-acetic Acid, Glycocol, $C_2H_3(NH_2)O_2$, can be made

by boiling glue with alkalies or acids, or by heating monochlor-acetic acid with ammonia, thus:

$$C_2H_3ClO_2 + 2NH_3 = C_2H_3(NH_2)O_2 + NH_4Cl.$$

Properties. Large, colorless, transparent crystals, of sweet taste.

This acid occurs in the body in hippuric and glycocolic acids, and in bile as sodium glycocholate.

Amines and amides are found in nature as the products of animal life in certain organic bases, constituting the nitrogenous end products of metabolism, such as urea, uric acid, creatin, &c. They are found as the products of vegetable life in alkaloids, and as products of putrefaction in ptomaines.

Amines are formed:

1. By destructive distillation, as aniline and pyridine.

2. By the action of ammonia on the chloride or iodide of alcohol radicals, thus:

$$C_2H_5Cl + NH_3 = NH_2(C_2H_5) + HCl.$$

3. By action of nascent hydrogen on cyanides of alcohol radicals, thus:

$$CH_3CN + 2H_2 = C_2H_5NH_2.$$

4. By action of nascent hydrogen on some nitro-compounds, thus:

$$C_6H_5NO_2 + 3H_2 = C_6H_5NH_2 + 2H_2O.$$

Formation of Amides by action of ammonia on chloride of acid radical, thus:

$$C_2H_3OCl + 2NH_3 = C_2H_3ONH_2 + NH_4Cl.$$

Further study of these bodies will be deferred, when they will be again taken up as alkaloids. Alkaloids containing carbon, hydrogen and nitrogen, are amines. Those containing carbon, hydrogen, nitrogen and oxygen, are amides.

CYANOGEN, (CN), Cy.

$N \equiv C - C \equiv N.$	$-C \equiv N.$	$-N \equiv C.$
Cyanogen molecule	Nitrils, or cyanides	Isocyanides, or carbylamines

Cyanogen is the first compound radical whose distinct existence was proved; it was discovered in 1811 by Gay-Lussac. The name, cyanogen, means "generator of blue," referring to the deep-blue compounds formed by this radical.

Occurrence in Nature. Cyanogen is not found free in nature to any great extent; it is said to occur in the gases issuing from volcanoes and iron furnaces. In combination, cyanogen is found in certain plants, such as the wild cherry, bitter almonds and peach kernels, which, in common with most of the members of the same family, contain the glucoside, amygdalin. Amygdalin, by action of the ferment emulsine in the presence of moisture, undergoes decomposition, forming hydrocyanic acid, glucose and other bodies. Cyanogen is said to occur as the sulphocyanate of potassium in the saliva in minute amount.

The chemical character of cyanogen is much like that of the halogens, and it was formerly classed as a member of this group; it forms salts resembling the salts of these elements, and is precipitated from solution by silver nitrate in the form of white cyanide of silver, which has much the appearance of silver chloride. The radical, when set free, forms a double molecule called di-cyanogen, $(CN)_2$, whose structure is represented above in the graphic formula.

Preparation. Though carbon and nitrogen cannot be made to combine directly, yet organic bodies containing carbon and nitrogen, when heated with caustic potash, yield potassium cyanide. When iron is present the ferrocyanide of potassium is formed. From these compounds the other cyanogen compounds are made.

Cyanogen $(CN)_2$ is prepared by heating mercuric or silver cyanide, thus:

$$Hg(CN)_2 + \text{heat} = Hg + (CN)_2.$$

Properties. A colorless gas, of pungent odor; soluble in water and alcohol, easily liquefied at $-20.7°$, and $-34°$ freezes to snow-white solid. Burns with purple-red flame.

Hydrocyanic Acid, HCN, *Prussic acid.* Discovered by Scheele in 1782. Found in water distilled from leaves and seeds of bitter almond, cherry and peach. Formed during destructive distillation of coal. Can be made in many ways:

1. By action of ammonia on chloroform:

$$CHCl_3 + NH_3 = HCN + 3HCl.$$

2. By heating ammonium formate:

$$NH_4HCO_2 = HCN + 2H_2O.$$

3. By action of dilute acids on metallic cyanides:

$$AgCN + HCl = HCN + AgCl.$$

4. By heating potassium ferrocyanide with dilute sulphuric acid:

$$2K_4Fe(CN)_6 + 6H_2SO_4 = K_2Fe_2(CN)_6 + 6KHSO_4 + 6HCN.$$

Properties. Pure hydrocyanic acid is a clear, colorless, mobile, volatile, inflammable liquid. The acid is miscible with water, alcohol or ether in all proportions; its specific gravity is .697, boiling point 26°, and it solidifies to a white feathery mass at $-15°$. It has the peculiar penetrating odor of bitter almonds.

Pure hydrocyanic acid is one of the most rapid and violent poisons known. When the vapor is inhaled, instant death ensues; small quantities produce headache, giddiness, nausea, dyspnœa and palpitation and depression of the heart. The minimum fatal dose is said to be .9 of a grain of the anhydrous acid, though much larger quantities have been recovered from.

The antidote is a mixture of a ferrous and a ferric salt with sodium carbonate, to form non-poisonous ferrocyanide of iron. Stimulants and artificial respiration must be resorted to—ammonia by inhalation and internally, and alcoholic stimulants—for the poison acts so rapidly there is no time to prepare the antidote.

Used in medicine as dilute acid, of 2 per cent. strength.

The dilute hydrocyanic acid can be made extemporaneously by action of six parts silver cyanide on five parts hydrochloric acid and fifty-five parts water, by weight, and decanting the clear liquid. It is a clear, colorless, acid liquid, having odor of peach kernels.

Potassium Cyanide, KCN. *Prepared* by action of hydrocyanic acid on alcoholic solution of caustic potash. Commercially made by heating a mixture of potassium ferrocyanide and potassium carbonate, and contains the cyanate:

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + Fe + CO_2.$$

The resulting mass is washed with water, and the salt crystallized from this solution.

Properties. A white, deliquescent, soluble salt, giving odor of hydrocyanic acid when moist. A solution of the salt undergoes decomposition on standing, and when heated is decomposed to ammonium and potassium carbonates. Forms double salts with heavy metals. It acts as a violent poison, like the acid.

Silver Cyanide, AgCN, precipitates as a white, insoluble powder when solutions of potassium cyanide and silver nitrate are mixed:

$$KCN + AgNO_3 = KNO_3 + AgCN.$$

It shows much resemblance to silver chloride, is slowly soluble in ammonia water, and gives cyanogen gas when heated.

Mercuric Cyanide, $Hg(CN)_2$, is obtained by dissolving mercuric oxide in hydrocyanic acid. It is a white, crystalline salt; soluble in water and alcohol. Gives cyanogen when heated.

Tests for Cyanides.

1. Silver nitrate gives a white precipitate of silver cyanide, insoluble in dilute nitric acid, soluble in ammonia water.

2. With ferrous and ferric salts, caustic potash and hydro-

chloric acid, gives a blue precipitate of Prussian blue, $Fe_43Fe(CN)_6$.

3. A dilute solution of picric acid, heated with hydrocyanic acid, gives a red color on cooling.

Cyanogen enters into combination with iron to form acid radicals, in which the usual chemical reactions of the metal are not obtainable, and the poisonous properties of cyanogen are absent. These acids are hydroferrocyanic acid, $H_4Fe(CN)_6$, in which iron is in the ferrous state; and hydroferricyanic acid, $H_3Fe(CN)_6$, in which iron is in the ferric state. These acids are known in the form of their salts.

Potassium Ferrocyanide, *Yellow Prussiate of Potash,* $K_4Fe(CN)_6.3H_2O$.

Preparation. By heating together refuse animal matter, potassium carbonate and iron scraps.

$$6KCN + Fe + 2H_2O = K_4Fe(CN)_6 + 2KOH + H_2.$$

The resulting mass is washed with water and the salt crystallized from this solution.

Properties. Large, soft, translucent, pale-yellow, odorless, non-poisonous, neutral crystals; soluble in water; insoluble in alcohol.

Tests for Ferrocyanides.

1. Blue precipitate with ferric salts—Prussian blue, $Fe_43Fe(CN)_6$.

2. Burn when heated on platinum foil, leaving ferric oxide.

3. With ferrous salts, a light blue precipitate, rapidly turning darker.

4. With cupric salts, a brownish red precipitate.

Potassium Ferricyanide, *Red Prussiate of Potash,* $K_3Fe(CN)_6$.

Preparation. By passing a stream of chlorine through solution of potassium ferrocyanide:

$$K_4Fe(CN)_6 + Cl = KCl + K_3Fe(CN)_6.$$

In this reaction, an atom of potassium is removed from the ferrocyanide, and the iron passes from the ferrous to the ferric state.

Properties. Red, prismatic crystals, soluble in water. The solution, upon standing in light, gradually forms the yellow prussiate of potassium; a similar change is caused by alkalies.

Cyanic and Sulphocyanic Acids, HCNO and HCNS, form cyanates and sulphocyanates. These salts are formed by the direct action of oxygen, or sulphur, on the alkali cyanides, when an atom of one or the other, as the case may be, enters the molecule. The acids are colorless liquids. *Potassium sulphocyanate* is used as a reagent for ferric salts, with which it gives a deep-red color, discharged by mercuric chloride. It is obtained by fusing ferrocyanide of potassium with sulphur and potash. It occurs in colorless, deliquescent, soluble crystals.

Iso-sulphocyanates. Constitution, as compared with sulphocyanates:

$$\underset{\text{Sulphocyanate}}{-S-C\equiv N} \qquad\qquad \underset{\text{Iso-sulphocyanate}}{-N=C=S}$$

Allyl Iso-sulphocyanate, C_3H_5NCS, is found as mustard seed oil. A clear liquid, of irritating odor, blisters skin.

Among organic cyanides two isomeric forms are known to exist, and these are denominated *cyanides or nitrils,* and *isocyanides, or carbylamines.* These two forms of cyanogen are represented graphically as follows:

$$\underset{\text{Nitrils or cyanides}}{R-C\equiv N} \qquad \text{and} \qquad \underset{\text{Isocyanides or carbylamines}}{R-N\equiv C.}$$

In the cyanides, nitrogen is trivalent; in the isocyanides, it is quinquivalent.

These compounds appear to be esters, but are not saponifiable by action of caustic alkalies.

Cyanides, or Nitrils may be made by heating together iodides of hydrocarbon radicals and potassium cyanide:

$$CH_3I + KCN = KI + CH_3CN.$$

Properties. Volatile liquids, or solids. When heated with water and mineral acids, or alkalies, yield organic acids.

Fulminic acid, $H_2N_2C_2O_2$. Seen in fulminate of mercury. Made by adding alcohol to a solution of mercury in nitric acid. Use in percussion caps.

Isocyanides, or Carbylamines. Formed by heating silver cyanide with iodides of hydrocarbon radicals.

$$CH_3I + AgCN = CH_3CN + AgI.$$

Characterized by a very disgusting odor.

Nitro Compounds contain the radical NO_2. Isomeric with the nitrous acid esters, but differ from them in not being saponifiable by alkalies. Structure:

$-O-NO$	$-NO_2$.
Nitrite	Nitro-compound

Some made by action of HNO_3 on hydrocarbon, as nitrobenzene.

Nitro-compounds contain NO_2. Nitroso derivatives contain, NO. Iso-nitroso derivatives contain, $=N-OH$.

AROMATIC HYDROCARBONS OR BENZENE SERIES.

Having studied the fatty, or open chain, hydrocarbons and their derivatives, we now take up the second of the two great divisions of organic bodies, viz., the aromatic hydrocarbons. These are called aromatic, because of the decidedly aromatic, and often pleasant, odor which many of them possess.

Differences between aromatic and fatty compounds. Aromatic hydrocarbons contain a large percentage of carbon, they usually have antiseptic properties, they are not foods. The substitution derivatives with nitric acid, sulphuric acid and bromine are easily formed and are quite stable, and the phenols, or alcohols, have an acid character and do not oxidize to form aldehydes. The amines are feebly basic. In all these respects aromatic hydrocarbons differ greatly from the fatty group. The members of one group cannot be converted into those of the other without an entire decomposition and reconstruction of the molecule, and, many times, this change cannot be accomplished at all.

Source. The great source of aromatic hydrocarbons is found in coal-tar, but they are formed also by the destructive distillation of other substances. Some of these bodies are formed in plants and may be obtained from the vegetable kingdom.

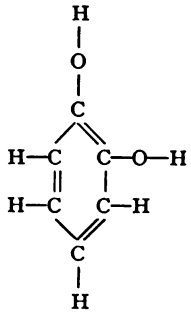
Constitution. No aromatic compound has less than six carbon atoms, and these are often referred to as the nucleus. The nucleus of the compound persists as a unit in spite of the other chemical changes which may take place in the molecule, and in this way the aromatic character of the substance is preserved. All the members of this group are derived from benzene by the replacement of hydrogen.

In benzene, C_6H_6, only one substance can be formed by

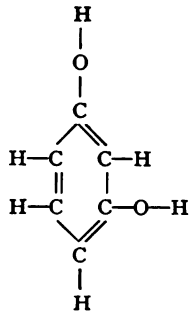
replacement of a single atom of hydrogen with a given radical, and it is therefore assumed that all the hydrogen is alike, or, in other words, that all the hydrogen atoms are similarly linked in the molecule. In order to give expression to this chemical structure, the molecule of benzene is represented by the graphic formula for the benzene ring, thus:

In this formula, it will be seen that the carbon atoms are linked in a closed chain, alternately by one and two points of attraction, leaving one for the attachment of a hydrogen atom. It will be seen further, that all the hydrogen is similarly linked, and as a result, when one atom is replaced by a given radical the same compound is always formed.

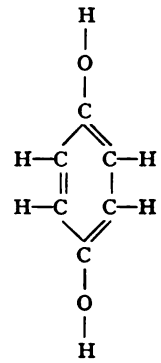
Such is not the case, however, when two hydrogen atoms of the ring are replaced by a given radical: in such an instance, the substance formed is capable of existing in three isomeric modifications, which seem to be dependent upon the relative positions of the replacing radicals. These three isomeric forms are named, Ortho-, Meta-, and Para-, indicating different relative positions in the benzene ring. When we replace two hydrogen atoms in the ring by two hydroxyl radicals, three isomeric forms result, the structure and names of which are given in the formulæ, thus:



Ortho-position.
Ortho-di-hydroxy
benzene



Meta-position.
Meta-di-hydroxy
benzene



Para-position.
Para-di-hydroxy
benzene

BENZENE SERIES.

The members here form an homologous series represented by the general formula, C_nH_{2n-6}. They are formed by replacement of hydrogen in benzene by the radical methyl, CH_3. Their names and structure are given in the following table:

TABLE OF AROMATIC HYDROCARBONS.

Benzene		C_6H_6.
Toluene	$C_6H_5CH_3$	or C_7H_8.
Xylene	$C_6H_4(CH_3)_2$	or C_8H_{10}.
Cumene	$C_6H_3(CH_3)_3$	or C_9H_{12}.
Tetra-methyl benzene.....	$C_6H_2(CH_3)_4$	or $C_{10}H_{14}$.
Penta-methyl benzene.....	$C_6H(CH_3)_5$	or $C_{11}H_{16}$.
Hexa-methyl benzene.....	$C_6(CH_3)_6$	or $C_{12}H_{18}$.

Many of these hydrocarbons occur in isomeric forms, thus greatly increasing their number.

The formation of derivatives of aromatic hydrocarbons follows the same rules that apply to the fatty group. Aromatic alcohols, aldehydes, acids, ethers and compound ethers are formed by replacement of hydrogen of the benzene nucleus by the appropriate radical, in each case. These chemical changes are usually accomplished, however, by indirect methods.

A benzene nucleus containing the marsh gas radical, CH_3, such as is seen in toluene, xylene, &c., partakes somewhat of the nature of a fatty hydrocarbon, because of the presence of this radical. The fatty portion, or side chain, of such a molecule, is capable of being oxidized into an alcohol, aldehyde and acid, as may be seen from the equations:

$C_6H_5CH_3$	$C_6H_5CH_2OH$	C_6H_5CHO	$C_6H_5CHO_2$.
Hydrocarbon	Benzyl alcohol	Benzoic aldehyde	Benzoic acid

Benzene, Benzol, C_6H_6.

Preparation. By distillation of coal-tar, products lighter and heavier than water are obtained, and these are separated by passing into water. Benzene is obtained by distillation of the "light oil," after it has been treated with caustic soda and sulphuric acid.

Benzene can be prepared, pure, by distilling a mixture of benzoic acid and calcium hydroxide, according to the equation:

$$C_6H_5HCO_2 + Ca(OH)_2 = CaCO_3 + H_2O + C_6H_6.$$

Properties. A colorless, volatile, inflammable liquid; peculiar ethereal odor; specific gravity, .884; boiling point, 80°; solidifies at 0°; insoluble in water. Benzene is a solvent for resins, fats, oils and many other bodies.

Toluene, Methyl Benzene, $C_6H_5CH_3$, or C_7H_8.

Toluene is found in coal-tar: it may be obtained by the dry distillation of balsam tolu.

Preparation of the members of the benzene series consists in heating the bromide of a given member of the series with the bromide of methyl and metallic sodium, when the next higher member of the series will be formed. This reaction may be utilized for the preparation of toluene, and is shown in the equation:

$$C_6H_5Br + CH_3Br + Na_2 = C_6H_5CH_3 + 2NaBr.$$

In properties, toluene shows some resemblance to fatty compounds, on account of the presence of the methyl radical. This radical is capable of being oxidized to benzoic acid.

Toluene is a clear, volatile liquid, much like benzene. It boils at 111°, and does not solidify at 0°—differing from benzene in these respects.

Xylene, Dimethyl Benzene, $C_6H_4(CH_3)_2$, is found in coal-tar. The ortho-, meta-, and para-forms are known.

Xylene is made from toluene by a reaction similar to the above, thus:

$$C_6H_4CH_2Br + CH_3Br + Na_2 = C_6H_4(CH_3)_2 + 2NaBr.$$

Xylene is a clear, colorless, volatile liquid: it yields phthalic acid, $C_6H_4(HCO_2)_2$, by oxidation.

Cymene, $C_6H_4CH_3C_3H_7$, or $C_{10}H_{14}$. (*Para-methyl-propyl benzene.*)

Cymene is found in the oil of thyme: it has been made by synthetic means.

This compound is a liquid, of pleasant odor, which boils at 175°; it is closely related to the terpenes, from which it may be obtained by heating with phosphoric oxide.

TERPENES, $C_{10}H_{16}$.

The terpenes constitute a class of isomeric hydrocarbons, formed by direct union of hydrogen to cymene. They are well known as the essential oils of juniper, turpentine, lemon, bergamot, &c. They possess strong antiseptic properties.

The terpenes undergo polymeric change with great ease by heating in closed tubes, or by the action of sulphuric acid. Sometimes this change occurs spontaneously, an example of which is seen in the conversion of oil of lemon into oil of turpentine by long standing.

Oxygen and hydrochloric acid combine directly with the terpenes: bromine and iodine, by dehydration, convert them into cymene.

Oil of Turpentine *is obtained* by distillation of the resin of various species of *Pinus* with steam.

Properties. A clear, colorless, thin, inflammable liquid; of characteristic, aromatic odor, burning taste; specific gravity, 0.855; boiling point, 160°; nearly insoluble in water; soluble in alcohol and ether; dissolves resins, oils, phosphorus, sulphur. When hydrochloric acid gas is passed through it, artificial camphor, $C_{10}H_{16}HCl$, separates as a solid.

Terebene is an optically inactive polymeric modification of above. Made by mixing turpentine with sulphuric acid and distilling; treating distillate with soda, and redistilling at 160°.

Resins are oxidized hydrocarbons, obtained from plants; they are divided, pharmaceutically, into *oleo-resins, gum-resins, and balsams.*

Oleo-resins contain resin and oil; gum-resins contain mucilage and oil; balsams are resinous bodies containing benzoic acid.

Properties. Resins are amorphous, brittle, insoluble in water, soluble in alcohol, ether and oils; they liquefy by heat, but decompose before volatilizing; they show the character of acids.

India rubber, or caoutchouc, is the dried milky juice of certain tropical plants. It consists of a mixture of hydrocarbons, chiefly, $C_{20}H_{32}$, $C_{10}H_{16}$, C_5H_8. *Properties.* Yellowish-brown; hard and tough when cold; insoluble in water and alcohol; soluble in ether, chloroform, bisulphide of carbon, and benzene. When heated, melts to thick liquid at 180°, and when cooled, remains soft and sticky for some time.

Vulcanized rubber contains seven to ten per cent. of sulphur. More elastic and flexible than crude form.

Hard rubber contains twenty to thirty-five per cent. sulphur, and sometimes a little white lead. Hard, tough, and capable of taking high polish.

Gutta percha. Dried juice of *Isonandra gutta.* Much like india-rubber. *Properties.* Hard, yellowish-brown, solid;

softens when heated; insoluble in water, alcohol, dilute acids, and alkalies; soluble in turpentine, bisulphide of carbon and chloroform.

Stearoptens or Camphors. *Obtained* by incising certain topical plants (*Cinnamomum camphorum*). Chemically, much like terpenes, but have oxygen in the molecule. Composition:

$$C_{10}H_{18}O \text{ and } C_{10}H_{16}O.$$

Properties. White, tough, crystalline masses; pleasant, characteristic odor; volatile; acts as a poison; soluble in alcohol, ether, chloroform, carbon bisulphide and oils; only slightly soluble in water. When heated with HNO_3 forms camphoric acid, $C_8H_{14}(HCO_2)_2$, a colorless, crystalline body, of acrid taste.

Camphor may be reduced to powder by the addition of a few drops of ether or alcohol.

Monobromated Camphor, $C_{10}H_{15}BrO$. Made by boiling camphor with bromine.

Properties. White, volatile, crystalline solid; odor and taste of camphor.

Menthol, Mint Camphor, $C_{10}H_{19}OH$. *Occurrence* in oil of peppermint, from which it separates on standing.

Properties. Clear crystals; nearly insoluble in water; soluble in alcohol; odor of peppermint; cooling, pungent taste.

Thymol, $C_{10}H_{14}O$, or $C_6H_3CH_3C_3H_7OH$ (*Methyl—propyl—phenol*). *Found* in oil of thyme.

Properties. Colorless, crystalline solid; odor of thyme; burning taste; melts at 50°; boils at 230°; nearly insoluble in water; soluble in alcohol. Used as an antiseptic.

Eucalyptol, $C_{10}H_{18}O$. Found in the volatile oil of *Eucalyptus globulus* and other species of eucalyptus. A colorless, aromatic, oily liquid.

PHENOLS AND PHENOL DERIVATIVES.

Definition of Phenols. Compounds formed by replacement of hydrogen of benzene by hydroxyl. Mono-, di- and tri-atomic, &c., like the fatty alcohols. Differ from latter by not forming aldehydes, or acids by oxidation.

Carbolic Acid, Phenol, Phenyl hydrate, Phenyl alcohol, C_6H_5OH. Crude acid *obtained* by distilling coal-tar at 170° to 190°; contains phenol, cresol and impurities. A reddish-brown liquid of disagreeable odor. *Pure acid* obtained by fractional distillation of crude variety.

Properties. Colorless, deliquescent, needle-shaped crystals, turning pink and then brown by long exposure; characteristic aromatic odor; corrosive, anæsthetic local action. By adding five per cent. of water converted into clear liquid; soluble in twenty parts water, in alcohol, glycerine, ether, chloroform and oils; melts at 35°; boils at 188°; specific gravity 1.065. An alcohol in chemical structure, but the hydrogen of the hydroxyl is replaceable by some metals; as by action of caustic potash or caustic soda to form phenolate of sodium, or potassium.

Largely used as an antiseptic. Acts as a poison. Antidote: Solution of sodium sulphate; mucilaginous drinks; stimulants.

Tests.

(Use an aqueous solution.)

1. Coagulates albumen and collodion.

2. Colors neutral solution of ferric chloride intensely and permanently violet-blue.

3. White precipitate with bromine water, of tribrom-phenol, $C_6H_2Br_3OH$.

4. Turns yellow on heating with nitric acid.

Creosote. Coal-tar creosote is chiefly carbolic acid. Official creosote is obtained from wood-tar, and best from beechwood-tar. Shows great resemblance to carbolic acid. Consists chiefly of guaiacol, $C_7H_8O_2$, and creosol, $C_8H_{10}O_2$.

Creosote is distinguished from carbolic acid by being less soluble in water (1 in 150), not coagulating collodion, not solidifying on cooling, and by high boiling point (205° to 215°).

Guaiacol, $C_6H_4OH.O(CH_3)$. A colorless liquid, strong, aromatic odor; soluble in alcohol, and ether. (*Creosol,* $C_6H_3.CH_3.OH.O(CH_3)$ or $C_7H_6(OH)(O.CH_3)$.)

Sulphocarbolic acid, *Sozolic acid, Aseptol, Phenol-sulphonic acid,* $C_6H_4HSO_3OH$.

Prepared by dissolving carbolic acid in strong sulphuric acid.

The sodium salt is made by dissolving Na_2CO_3 in the acid, when the hydrogen of HSO_3 is replaced by sodium, thus: $C_6H_4NaSO_3OH$.

A white, soluble crystalline salt.

Sulphonic acid is viewed as formed from H_2SO_3, by replacing one hydrogen atom by organic radicals.

Ichthyol is a brown, tar-like liquid, having a disagreeable odor; it is obtained by distilling a mineral found in the Tyrol.

Resorcin, Resorcinol, *Meta-dihydroxy-benzene,* $C_6H_4(OH)_2$. A diatomic phenol. *Formed* by fusing resins, as, galbanum and asafœtida, with caustic alkalies. May be made synthetically from benzene.

Properties. White, or reddish-brown, crystalline powder, soluble in water, sweetish taste; fuses at 118°; boils at 276°.

Pyrogallic Acid, *Pyrogallol,* $C_6H_3(OH)_3$. *Prepared* by heating gallic acid to 200°, when CO_2 escapes.

Properties. Forms colorless, needle-shaped crystals; melts at 131°; soluble in water, ether and alcohol. Alkaline solutions of pyrogallic acid absorb oxygen, and turn red, then brown. Gives a yellow color with nitric acid, which turns brown. Acts as a strong reducing agent.

Oil of Bitter Almonds, *Benzaldehyde,* C_6H_5COH. Easily oxidized to benzoic acid. Does not occur free.

Formed by fermentation of *amygdalin,* a glucoside, found in bitter almonds, wild cherry, kernels of peaches, &c., by action of ferment *emulsin,* in presence of water; forming glucose, oil of bitter almonds and hydrocyanic acid.

Prepared by maceration of bitter almonds with water, and distilling, and thus contains hydrocyanic acid.

Properties. Colorless, oily liquid, of peculiar odor. Poisonous properties due to presence of HCN. Bitter almond water has one part oil bitter almonds to 999 of water.

Benzoic Acid, $C_6H_5CO_2H$, or $H.C_7H_5O_2$.

Occurrence in nature in resinous substances, called balsams, and in the urine of herbivorous animals.

Preparation. From the resins by distillation. Artificial preparation, by action of chlorine upon warm toluene, to form tri-chlormethyl-benzene, and action of water, under pressure, upon this compound, thus:

$$C_6H_5CH_3 + 6Cl = C_6H_5CCl_3 + 3HCl,$$
$$C_6H_5CCl_3 + 2H_2O = C_6H_5CO_2H + 3HCl.$$

Properties. White, shining, scaly crystals; slight aromatic odor of benzoin; acid reaction; slightly soluble in water; soluble in ether, alcohol and oils.

Neutralized with an alkali and treated with neutral ferric chloride, forms a reddish precipitate.

Ammonium, Sodium and Lithium Benzoate. Formed by neutralizing benzoic acid with ammonium and sodium hydroxide, and lithium carbonate. All three are white, soluble salts.

Phthalic Acid, $C_6H_4(CO_2H)_2$. A dibasic aromatic acid. *Formed* when ortho-xylene, $C_6H_4(CH_3)_2$, is oxidized by nitric acid, or potassium permanganate. *Occurs* in short, prismatic crystals; soluble in water, alcohol and ether. It melts at 184°, and when heated above this point it loses water and is converted into the anhydride, according to the equation:

$$C_6H_4(CO_2H)_2 - H_2O = C_6H_4C_2O_3.$$

Phthalic anhydride, by action of phenol and sulphuric acid, forms *phenol-phthalein,* thus:

$$C_8H_4O_3 + 2C_6H_5OH = H_2O + C_{20}H_{14}O_4.$$

Phenol-phthalein forms colorless, needle-shaped crystals; insoluble in water, soluble in alcohol. Solution of this salt is purplish-red in alkaline medium, colorless in acids. It is used as an indicator in analysis.

Phenol acids contain at least one OH radical attached to the benzene ring, and carboxyl in addition. They are called oxyacids, because of the additional oxygen of this hydroxyl.

Salicylic acid, Oxybenzoic acid, $C_6H_4(OH)(CO_2H)$, or $H.C_7H_5O_3$.

Occurrence in Nature. As methyl ester, in oils of wintergreen, and birch. May be obtained by fusing caustic potash with indigo, or salicin.

Preparation. By first forming sodium phenolate, thus:

$$C_6H_5OH + NaOH = C_6H_5ONa + H_2O.$$

The sodium phenolate is dried and acted upon by CO_2, in closed vessels, at temperature of 130°, and the resulting compound is treated with hydrochloric acid, as shown in the equations:

$$2C_6H_5ONa + CO_2 = C_6H_4NaOCO_2Na + C_6H_5OH.$$

$$C_6H_5ONaCO_2Na + 2HCl = C_6H_4OHCO_2H + 2NaCl.$$

Properties. Fine, needle-shaped crystals, white color, sweetish acrid taste, acid reaction. Slightly soluble in water; soluble in alcohol and ether. Fuses at 158°; volatilized in a current of steam, or at 200°. Use as antiseptic and preservative.

Tests.

1. Solution with ferric chloride gives violet color.
2. Cupric sulphate gives green color.
3. Dissolve in methyl alcohol, and add one-fourth volume

sulphuric acid, and heat; odor of methyl salicylate develops.

Sodium Salicylate is obtained by dissolving sodium hydroxide in salicylic acid. It is a soluble salt, of sweetish taste, and is much used in medicine.

Methyl Salicylate, $CH_3C_7H_5O_3$. Occurs as oil of wintergreen, in *Gaultheria procumbens.* Made by heating salicylic acid, methyl alcohol, and sulphuric acid together. It is a clear liquid, of fragrant odor.

Phenyl Salicylate, Salol, $C_6H_5C_7H_5O_3$. *Made* by heating together sodium phenolate, sodium salicylate, and phosphorus oxychloride.

Properties. A white, crystalline powder; nearly insoluble in water; soluble in ether, alcohol, benzene and oils (fatty and essential); peculiar odor, slight taste; fuses at 42°. Used as antiseptic, analgesic, and antipyretic.

Salol is decomposed, with liberation of phenol, by action of caustic potash.

Gallic Acid (*Trioxy-benzoic acid*), $C_6H_2(OH)_3CO_2H$, or $H.C_7H_5O_5$.

Prepared from nut-galls by moistening and exposing to the air for about six weeks, for fermentation, in which tannic acid is converted into gallic acid, extracting the mass with boiling water, and crystallizing. May be obtained from tannic acid by boiling with diluted acids or alkalies.

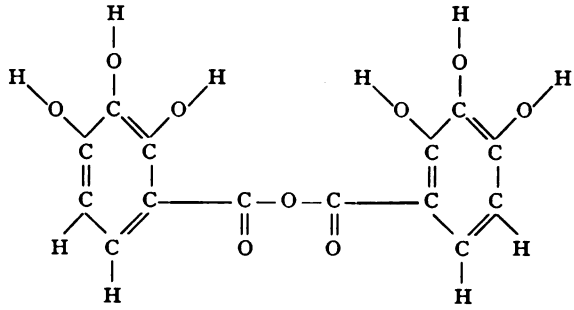
Properties. A white solid, in silky, needle-shaped crystals; astringent, acid taste, acid reaction; soluble in one hundred parts cold, three parts hot water; soluble in alcohol, only slightly soluble in ether and chloroform.

Tests.

1. Gives a bluish-black precipitate with ferric salts.
2. Does not coagulate albumen nor precipitate alkaloids, gelatine or starch.

3. With potassium cyanide gives a rose color.

Tannic Acid, $C_{14}H_{10}O_9$. (*Digallic acid.*) Chemical structure represented by the graphic formula.



Occurrence in Nature. Tannic acid occurs in many plants, in varying forms, but it is usually obtained from nut-galls.

Preparation. By extracting powdered nut-galls with commercial ether, and allowing the acid to crystallize from the solution.

Properties. Light-yellowish, amorphous powder, or scales, very astringent; acid reaction; freely soluble in water. When boiled with dilute alkalies or acids it forms gallic acid, by taking up water.

Tests.

1. Ferric chloride gives bluish-black precipitate, soluble in excess with greenish color.
2. Solution caustic potash gives brown color.
3. In weak solution with lime water, a white precipitate forms, which turns blue with excess of $Ca(OH)_2$.
4. Precipitated by gelatine, tartar-emetic, albumen, or alkaloids.

NITROGEN COMPOUNDS OF BENZENE.

The Nitro-derivatives of Benzene are formed by the action of strong nitric acid upon the aromatic hydrocarbons, by which

means the hydrogen of the benzene ring is replaced by the radical NO_2. These compounds usually enter into solution in the strong nitric acid causing their formation, and may be precipitated by the addition of water. This action of nitric acid may be represented thus:

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Nitric acid}}{NO_2OH} = \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O.$$

$$\underset{\text{Toluene}}{C_6H_5CH_3} + NO_2OH = \underset{\text{Nitro-toluene}}{C_6H_4NO_2CH_3} + H_2O.$$

These compounds are named mono-, di- and tri-nitro compounds, &c., according to the number of the replacing radicals.

This replacement of hydrogen takes place in the hydrogen of the benzene nucleus, and not in the side group. The number of the replacing radicals depends upon the strength of the acid and the length of time it is allowed to act.

General Properties. The nitro-compounds are usually pale-yellow or yellowish liquids, that can be distilled in a current of steam; or, as is the case with the higher derivatives, yellow, needle-shaped or prismatic crystals; heavier than water and insoluble, but soluble in alcohol, ether and strong acetic acid.

All the nitro-compounds are reduced by the action of nascent hydrogen, in acid solution, to the corresponding amido compounds, in which hydrogen takes the place of oxygen; thus, $C_6H_5NO_2$ becomes $C_6H_5NH_2$. This change may be effected by the action of tin on hydrochloric acid, in the presence of the nitro-derivatives. They are largely used for making amido-compounds.

Nitro-benzene, $C_6H_5NO_2$. Formed by adding benzene, slowly, to cooled nitric acid as long as the hydrocarbon seems to dissolve. After standing for some time, the nitro-benzene is separated by adding water, washing with water and with weak caustic soda, and distilling with steam.

Properties. A light-yellowish liquid, with an odor of bitter almonds; boils at 205°, and crystallizes at 3°. Used for making aniline, or phenyl-amine, and as perfumery for soap by the name, *essence of mirbane.* Highly poisonous.

Antidote: Empty the stomach and use ammonium carbonate, or aromatic spirit of ammonium, cold to the head and electricity.

Dinitro-benzene, $C_6H_4(NO_2)_2$, is formed when benzene is added to a mixture of nitric and sulphuric acids and heated to boiling. It is solid and crystalline.

Trinitrophenol, $C_6H_2(NO_2)_3OH$. (*Picric acid, carbazotic acid.*) Not a true nitro-benzene, but a nitro-phenol. Mono- and di-nitro-phenols known, but this is the only important one. Formed by action of fuming nitric acid on many organic bodies, as indigo, silk, leather, wool, &c.

Prepared, usually, by slowly adding carbolic acid to fuming nitric acid.

Properties. It forms pale-yellow scales, or needles. It is slightly soluble in water, alcohol, and ether. It melts at 122.5°, and can be sublimed when carefully heated, but when rapidly heated explodes. Some of its salts form beautiful crystals, but they are very explosive by heat or concussion. It is used as a yellow dye for silk and wool; is poisonous when taken internally in sufficient dose.

AMIDO DERIVATIVES OF BENZENE.

It is necessary to remember, in studying these compounds, that they may be looked upon from two points of view: First, as benzene in which one or more of the hydrogen atoms have been replaced by the radical, NH_2, when the name would be *amido-benzene;* second, as ammonia in which one, two or all three hydrogen atoms have been replaced by the radical, C_6H_5, and named *phenyl-amine.* Furthermore, they are named *mon-amines, di-, tri-, tetra-amines,* &c., according to the number of

the radical NH_2; or *primary, secondary* and *tertiary amines,* according to the number of C_6H_5, replacing hydrogen in ammonia (NH_3). For example, phenyl-amine, $C_6H_5NH_2$, is a primary amine; diphenyl-amine, $(C_6H_5)_2NH$, is a secondary amine, &c.

Aniline, Phenyl-amine, $C_6H_5NH_2$, *is a primary monamine* —primary, because of one C_6H_5; monamine, because of one NH_2. First obtained by dry distillation of indigo. Occurs in coal-tar, and bone-oil.

Prepared by action of nascent hydrogen on nitro-benzene, $C_6H_5NO_2$, when hydrogen replaces the oxygen to form $C_6H_5NH_2$.

Properties. A colorless, oily liquid; turning yellow or brown on exposure to air. Peculiar odor, bitter taste; poisonous. Slightly alkaline and combines with acids, with retention of hydrogen like ammonia, to form salts.

Aniline dyes are made from impure aniline containing toluidine, by the action of oxidizing agents, as arsenous, and arsenic oxides, chromic or nitric acid or hypochlorites, forming the various beautifully colored compounds.

Diphenyl-amine, $(C_6H_5)_2NH$, is a secondary monamine, obtained by destructive distillation of tri-phenyl-rosaniline (or aniline blue).

Properties. White scales, having an agreeable odor of flowers, and a burning, aromatic taste. It is nearly insoluble in water, soluble in alcohol, ether and petroleum naphtha. Dissolved in strong sulphuric acid, it is colored blue by nitric or nitrous acid, and is used as a reagent in water analysis.

Meta-phenyl-diamine, $C_6H_4(NH_2)_2$. Made by the action of reducing agents on meta-dinitro-benzene. Forms grayish crystals; nearly insoluble in water; soluble in alcohol and ether. Basic properties. Forms a yellow color, with traces of nitrous acid. Used as reagent.

Sulphanilic Acid, *Aniline-para-sulphonic acid,* $C_6H_4NH_2$-SO_3H. Made by heating aniline with fuming sulphuric acid. A colorless, crystalline solid; slightly soluble in water. It is used in obtaining the diazo-reaction in urine of typhoid fever, measles and tuberculosis. This test is applied by dissolving the above compound in water and hydrochloric acid and adding to urine, and then adding $NaNO_2$ solution, and ammonia. Normal urine, yellow; in above diseases, red color forms. Presence of phenol, gives a red color.

Acetanilide, Antifebrine, Phenyl-acetamide, $C_6H_5NHC_2$-H_3O. Anilides are formed by replacement of hydrogen of amidogen in the amido-compounds, by alcohol or acid radicals. Named alcohol-anilides and acid-anilides.

Preparation. By boiling aniline with glacial acetic acid in such a manner that the vapors are recondensed, for two days, until a drop taken out solidifies on cooling. The product is then subjected to fractional distillation, when water first distills off, and that which comes over at 295° is collected.

Properties. Colorless, odorless, scaly crystals; nearly insoluble in cold water; soluble in hot water, alcohol and ether; neutral in reaction. *It is decomposed by hydrochloric acid to aniline and acetic acid.*

Exalgin, Methyl-acetanilide, $C_6H_5N.CH_3.C_2H_3O$. Made by the action of methyl iodide upon sodium acetanilide.

Properties. Crystalline needles; nearly insoluble in water; soluble in alcohol; fuses at 100°; boils at 250°.

Benzanilide, $C_6H_5CO.NHC_6H_5$, is sometimes used in medicine.

Amido-phenols, $C_6H_4.OH.NH_2$, are formed by the action of reducing agents (H) on the corresponding nitro-phenol (C_6H_4-$OHNO_2$), when hydrogen takes the place of oxygen. The ethyl ethers of amido-phenols, formed by replacing hydrogen of the hydroxyl by C_2H_5 —$C_6H_4O.C_2H_5NH_2$—, are called

"phenetidines." When para-phenetidin, $C_6H_4OC_2H_5NH_2$, is treated with glacial acetic acid, the radical of this acid is introduced, taking the place of hydrogen in amidogen, and forming *para-acet-phenetidin* ($C_6H_4OC_2H_5NHC_2H_3O$). This compound is used in medicine under the name *phenacetine.*

Properties. It forms white, lustrous crystals; odorless and tasteless; nearly insoluble in water; soluble in alcohol.

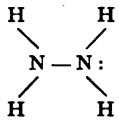
Diazo and Azo compounds contain the radical, $-N=N-$. In the diazo compounds this radical links together a hydrocarbon radical and an acid radical, thus: $C_6H_5-N=N-Cl$, diazo-benzene chloride. In azo compounds it links two hydrocarbon radicals together, thus: $C_6H_5-N=N-C_6H_5$, azobenzene.

Diazo-compounds are formed by the action of nitrous acid upon aromatic amines, in acid solution:

$$C_6H_5NH_2HCl + OHNO = C_6H_5N_2Cl + 2H_2O.$$

They are colorless, crystalline, and sometimes explosive. Soluble in water; insoluble in ether.

Hydrazines are derivatives of hydrazine, or N_2H_4, or NH_2NH_2,



Formed from it by replacement of hydrogen by hydrocarbon radicals.

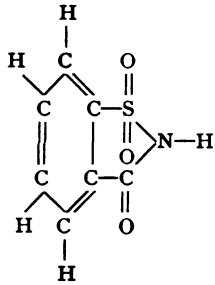
Phenyl Hydrazine, $C_6H_5NH\text{-}NH_2$. *Prepared* by reduction of diazo-benzene chloride, by nascent hydrogen:

$$\underset{\text{Diazo-benzene chloride}}{C_6H_5N_2Cl} + 2H_2 = \underset{\text{Phenyl Hydrazine hydrochloride}}{C_6H_5N_2H_3.HCl}.$$

Properties. A colorless, crystalline solid; fuses at 23° to an oily liquid. It is strongly basic, a powerful reducing agent, and reduces Fehling's solution in the cold. It is used as a re-

agent, as it combines with aldehydes and ketones, and hence, with sugars, to form crystalline compounds known as *hydrazones* and *osazones;* used also in making antipyrine.

Saccharine, Anhydro-ortho-sulphamine-benzoic Acid, $C_6H_4CO.SO_2NH$. Formed from benzoic acid, $C_6H_5CO_2H$, by elimination of water and introduction of the radicals SO_2, and NH. Two hydrogen atoms of ammonia, and two hydrogen atoms of benzene, are replaced by SO_2 and CO, thus:



Properties. A white powder, slightly soluble in water (solution acid reaction), soluble in alcohol and ether. Slight odor of bitter almonds, very sweet taste; 280 times sweeter than cane-sugar.

Antipyrine, *Phenyl-dimethyl-pyrazalon,* $C_{11}H_{12}N_2O$.

Properties. A white, crystalline bitter powder; freely soluble in water and alcohol. Forms a green, poisonous compound with nitrous acid, the same change taking place, after a time, with "sweet spirit of nitre."

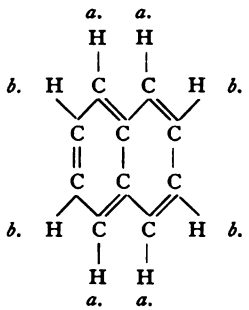
COMPOUNDS WITH CONDENSED BENZENE NUCLEI.

In the aromatic hydrocarbons hitherto considered the single, or uncondensed, benzene molecule has formed the nucleus, the general formula of which is C_nH_{2n-6}. Other aromatic hydrocarbons are well known, in which two and three benzene molecules are condensed into a single nucleus. These compounds are distilled at the higher boiling point of coal-tar; they contain a large percentage of carbon as compared to the hydro-

gen; and they form two homologous series. The compounds forming these series are Naphthalene and Anthracene; and both of them may be regarded as derivatives of benzene, since by their oxidation, phthalic acid and benzoic acid are formed, respectively.

Naphthalene, Coal-tar Camphor, $C_{10}H_8$, forms the homologous series of hydrocarbons having the general formula C_nH_{2n-12}, by replacement of its hydrogen with the radical methyl, CH_3.

The molecular structure of naphthalene is that of a double condensed benzene ring, in which two carbon atoms are common to both rings. This structure is shown in the graphic formula:



There are two kinds of carbon in the naphthalene molecule: one kind is attached to carbon which is found in one ring only; the other kind is attached to carbon which is common to both rings. As a result of this structure of the naphthalene nucleus, two isomeric forms are produced when hydrogen is replaced by a single radical; these are known as the alpha and the beta forms. There are four alpha positions, and four beta positions, in the naphthalene molecule, and these are represented in the above graphic formula by the letters *a* and *b*.

Naphthalene is formed by the destructive distillation of many organic bodies. It is prepared by distilling coal-tar at 180°

to 220°, treating the product with caustic soda and sulphuric acid, and distilling with watery vapor.

In properties, naphthalene is a white, shining, scaly, crystalline solid; having a penetrating odor, burning taste; slightly soluble in water; soluble in alcohol, ether or chloroform. It is used in medicine as an intestinal antiseptic, and as an insecticide in the form of "moth-balls."

Naphthol, Naphtol, $C_{10}H_7OH$, is the hydroxyl derivative of naphthalene. The alpha and beta forms are known.

Beta-Naphthol is the one used in medicine. It forms shiny, crystalline plates; has the odor of carbolic acid, a burning taste, and is soluble in alcohol, ether, chloroform and oils; only slightly soluble in water.

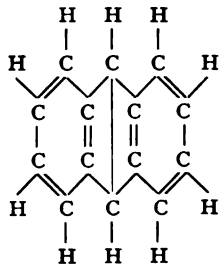
Santonine, $C_{15}H_{18}O_3$. While the chemical structure of santonine is not understood, it is known to be related to naphthalene.

Santonine is obtained from *Artemisia santonica.* It is prepared by extracting with alcohol and lime water, and liberating santonine by adding an acid.

Properties. Colorless, prismatic crystals, which turn yellow by exposure to light; slightly soluble in water; soluble in alcohol or ether; colors the urine dark when administered internally. Such urine when heated turns red; the red color is destroyed by an acid and restored by an alkali.

Anthracene, $C_{14}H_{10}$, forms an homologous series of hydrocarbons, having the general formula C_nH_{2n-18}, by replacement of its hydrogen by the radical methyl, CH_3.

The molecular structure of anthracene is that of three condensed benzene nuclei, as shown in the graphic formula:



Anthracene is obtained by the fractional distillation of coal-tar above 300°.

The pure hydrocarbon occurs in the form of crystalline plates, of white color, with a blue fluorescence; it melts at 212°, and boils at 360°; it is slightly soluble in alcohol or ether; easily soluble in hot toluene or benzene.

When anthracene is oxidized, it yields a compound called *anthraquinone;* reducing agents convert it into *anthracene-hydride.*

Anthracene is used largely in the preparation of *alizarine* and other artificial coloring agents.

COMPOUNDS CONTAINING NITROGEN IN THE BENZENE NUCLEUS.

Pyridine Bases.

By destructive distillation of bones a tar-like substance is formed from the bone gelatine, called bone-oil, or Dippel's oil. This liquid furnishes a number of basic substances among which are the pyridine bases, some of which can also be obtained from coal-tar.

The pyridine bases form an homologous series, derived from pyridine, the names of which are given in the following table:

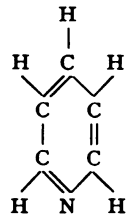
Pyridine, C_5H_5N,	Collidine, $C_8H_{11}N$,
Picoline, C_6H_7N,	Parvoline, $C_9H_{13}N$,
Lutidine, C_7H_9N,	Coridine, $C_{10}H_{15}N$.

In properties, these bodies are liquids, of disagreeable pungent odor; they resemble ammonia, to which they are closely related; and they are capable of forming salts with acids.

The pyridine bases are separated from bone-oil by shaking with sulphuric acid, with which they form salts; the salts are dissolved in water, decomposed by adding caustic soda and removed by distillation.

Pyridine, C_5H_5N, is the parent substance of the pyridine bases. In chemical structure, it consists of a benzene ring in

which a carbon and hydrogen atom have been replaced by nitrogen. This structure is shown in the graphic formula, thus:



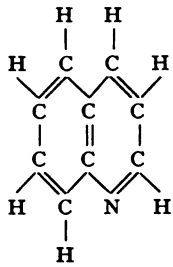
The other members of the series, given above, are formed by replacing hydrogen of the ring by the radical CH_3.

Properties. Pyridine is a colorless liquid; tarry odor; pungent taste; boiling point 116°; specific gravity .98; soluble in water; hygroscopic. It forms salts with acids by direct union and retention of hydrogen.

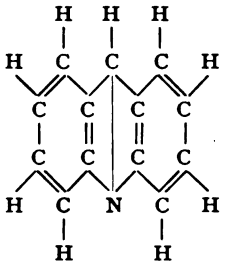
Pyridine is found in tobacco-smoke, being produced by the destructive distillation of tobacco in smoking. The effect of smoking, upon the heart and nervous system, is largely due to pyridine absorption.

It has been used in medicine as a remedy for asthma.

Naphthalene and anthracene furnish nitrogen derivatives analogous in structure to those derived from benzene. They are basic bodies obtained from bone-oil and coal-tar. Their structure is represented in the following graphic formulas, showing the replacement of a hydrogen and a carbon atom in naphthalene and anthracene by nitrogen. These nitrogen derivatives have been named Quinoline and Acridine.

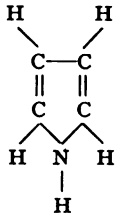


Quinoline.



Acridine.

Pyrrole, C_4H_4NH, has the molecular structure represented in the following graphic formula, thus:



Pyrrole is a feebly basic liquid, obtained from bone-oil and coal-tar. It boils at 130°; has an odor resembling chloroform, and is insoluble in water, but soluble in alcohol, ether or dilute acids. It is used for making iodol.

Iodol, C_4I_4NH, is formed from pyrrole by replacing hydrogen with iodine.

It is prepared by dissolving pyrrole in alcohol, adding iodine, and then adding an oxidizing agent.

Properties. Grayish-brown or yellowish powder; odorless; tasteless; soluble in alcohol or ether; nearly insoluble in water. It decomposes at 150°, evolving iodine.

Iodol is largely used as an odorless substitute for iodoform in surgical dressings.

ALKALOIDS.

Many plants, and especially those having medicinal or poisonous properties, contain basic principles, in which the physiological properties of the plant reside. These principles are feebly alkaline in reaction and are therefore called alkaloids, this term meaning alkali-like.

Alkaloids are feebly basic substances containing nitrogen and representing the active principles of plants. In chemical nature, they are closely related to pyridine and quinoline, from which some of them have been prepared by artificial means. Since they all contain the residue of the ammonia radical they are regarded as members of the amine and amide group, and as such, they may be divided into two classes, viz.: Liquid volatile alkaloids, or amines, containing carbon, hydrogen and nitrogen; and solid non-volatile alkaloids, or amides, containing carbon, hydrogen, nitrogen and oxygen.

The resemblance of alkaloids to ammonia is clearly shown in their basic properties; their power to combine with acids to form salts in which the hydrogen is retained; their precipitation with perchloride of platinum, or alkaline potassium-mercuric iodide solution.

In naming the salts of alkaloids, the same rules are followed as in other cases, except for the halogen acids. Instead of using the terms chloride, bromide, or iodide, for the alkaloidal salts of these acids, the terms hydrochloride, hydrobromide and hydriodide are employed; therefore, instead of speaking of morphine chloride, the term morphine hydrochloride is used. The termination *ine* is used in naming the alkaloids.[1]

The alkaloids are found in all parts of plants, but they occur most frequently in the seeds, stems, leaves and bark. Sometimes a given alkaloid is found in different species of the same family of plants, and again, different alkaloids are found in

[1] See U. S. P., 1900.

the various parts of the same plant; in the latter case, however, the alkaloids show resemblance in chemical character and physiological properties.

The alkaloids do not usually occur free in nature, but they are found as salts with vegetable acids. Morphine occurs combined with meconic acid; quinine, with kinic acid, &c.

General Method of Preparation. The vegetable substance is disintegrated and extracted with acidulated water, which dissolves out the alkaloid. To this solution is added an alkali, which precipitates the alkaloid, and, if it be volatile, it is separated by distillation. If not volatile, the resulting precipitate is collected, washed and purified by redissolving in acidulated water and reprecipitating, or it may be purified by crystallizing from alcohol.

General Properties. The alkaloids as a class are powerful in their physiological action: many of them are intensely poisonous, such as strychnine and atropine, while a few are comparatively harmless, such as quinine and caffeine.

Most of the alkaloids have a bitter taste; the greater number are solid non-volatile; some are liquid and volatile, having a disagreeable odor; the solid ones are white and usually crystalline. They have an alkaline reaction, and unite with acids to form well defined crystallizable salts.

The Free Alkaloids are usually insoluble in water, but soluble in alcohol, ether, chloroform, benzene or acetic ether. *The alkaloidal salts* are usually soluble in water or alcohol, but insoluble in ether, chloroform or benzene.

General Tests and Precipitants. The alkaloids are precipitated from solution by the addition of solution of caustic alkalies, tannic acid, picric acid, potassium-mercuric iodide, perchloride of platinum and chloride of gold.

Mayer's Reagent is made by dissolving 49.8 gm. potassium iodide, and 13.546 gm. mercuric chloride, in water to make 1000 cc. It gives a white, or yellowish precipitate.

Iodine Solution, or Wagner's Reagent, is a solution of iodine and potassium iodide in water, of convenient strength—about 20 gm. iodine and 50 gm. iodide of potassium in 1000 cc. of water. This reagent gives a red, or reddish-brown precipitate.

Many of the alkaloids give beautiful color reactions with oxidizing agents.

In Poisoning by Alkaloids, emetics and the stomach-pump should be used. Chemical and physiological antidotes are employed: the former to produce an insoluble, or harmless compound, with the alkaloid; the latter to counteract its physiological action. The general chemical antidote is tannic acid.

Liquid Volatile Alkaloids.

Conine, $C_8H_{17}N$. *Source:* Conium maculatum (Hemlock).

Properties. Colorless, oily liquid; disagreeable odor; acrid taste; becomes thick and resinous by exposure. Gives vapor to air, which forms white fumes with hydrochloric acid, like ammonia.

Sparteine, $C_{15}H_{26}N_2$. *Source: Scoparius* (Broom top).

Properties. Colorless, oily liquid. Forms the sulphate by union with sulphuric acid; a crystalline, soluble solid.

Nicotine, $C_{10}H_{14}N_2$. *Source:* Obtained from tobacco; the leaves of which contain from two to eight per cent. Colorless, oily liquid, turns brown. Very poisonous.

Solid Non-Volatile Alkaloids.

Opium is the concrete, milky exudation, obtained by incising the unripe capsules of *Papaver somniferum* in the Orient. It contains gum, fat, albumen, wax, glucose, volatile matter, meconic acid, morphine, codeine and many other alkaloids.

It should contain not less than 9 per cent. of morphine. Dried opium should have 13 to 15 per cent. morphine.

Deodorized opium is opium exhausted with ether, to remove

narcotine, and the weight made up to the original by adding sugar of milk.

Morphine, $C_{17}H_{19}NO_3.H_2O$. *Properties.* Short, transparent, white, prismatic crystals; bitter taste; soluble in alcohol; slightly soluble in water; nearly insoluble in ether and chloroform; alkaline in reaction, and combines with acids to form crystalline salts.

The *acetate, hydrochloride* and *sulphate* are used in medicine; they are white and soluble.

Apomorphine, made by heating morphine with excess of hydrochloric acid under pressure. A white salt, turns green when exposed to air. Used as an emetic.

Tests for Morphine.

1. With nitric acid, a red color forms; gradually turns yellow.
2. Blue color with neutral ferric chloride.
3. Morphine, sugar and sulphuric acid give a red color.
4. Solutions are precipitated by alkali hydroxides; soluble in excess; except ammonia water.

Codeine, $C_{18}H_{21}NO_3.H_2O$. *Properties.* White, crystalline powder; soluble in alcohol and chloroform, slightly soluble in water. Neutral; bitter.

Tests for Codeine.

1. Solution with chlorine water and ammonia water gives yellowish-red color.
2. Dissolved in sulphuric acid, and warmed with ferric chloride, gives deep blue.

Meconic Acid, $C_4OH(CO_2H)_3$. *Preparation.* By extracting opium with water, neutralizing with $CaCO_3$, precipitating with $CaCl_2$ and adding HCl.

Properties. White, crystalline, soluble in water and alcohol.

Test.

Ferric chloride gives blood-red color, not affected by mercuric chloride; thus differing from sulphocyanide of potassium. Its presence indicates opium in case of poisoning.

Cinchona Bark, to be official, must contain not less than five per cent. of total alkaloids, and not less than 2.5 per cent. of quinine. The alkaloids are in combination with *kinic acid.* It is obtained from various species of cinchona. Its most important alkaloids are quinine, quinidine, cinchonine and cinchonidine.

Quinine, $C_{20}H_{24}N_2O_2.3H_2O$. *Properties.* White, flaky, crystalline or amorphous powder permanent in the air; very bitter taste. Soluble in alcohol, ether, chloroform, carbon bisulphide, benzene, ammonia water and dilute acids; nearly insoluble in water. At 125°, it loses water of crystallization and becomes a resinous mass of anhydrous quinine.

Quinine Sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4.7H_2O$. Formed by union of two molecules of quinine with one of sulphuric acid.

Properties. White, fine, needle-shaped crystals; absorbs or gives up moisture, as air is moist or dry; very bitter; soluble in alcohol, glycerine; only slightly soluble in water; dissolves in acidulated water with fluorescence.

Bisulphate of Quinine is formed when the sulphate is dissolved in excess of sulphuric acid, and contains a molecule of the alkaloid united to a molecule of the acid, thus:

$$C_{20}H_{24}N_2O_2.H_2SO_4.$$

Properties. Colorless, transparent, needle-shaped crystals; soluble in water.

The *Valerianate, Hydrochloride* and *Hydrobromide* are used in medicine; and they are freely soluble in water, except the valerianate, which is sparingly soluble.

Tests for Quinine.

1. Solutions of quinine in acidulated water, with chlorine water and ammonia water, give a green color.

2. The above, to which a crystal of potassium ferrocyanide has been added before the ammonia water, gives a pink color which soon turns red.

3. Quinine is precipitated white by ammonia water, but dissolves in excess.

4. Fluorescence in acid solution by reflected light.

Quinidine. Isomeric form of quinine, and like it in properties. Differs in being precipitated from neutral solution by potassium iodide.

Cinchonine and Cinchonidine are isomeric. Formula, $C_{19}H_{22}N_2O$. In properties they are like quinine. Cinchonine may be distinguished from quinine by the insolubility of the precipitate formed by ammonia water in an excess of the reagent. Cinchonidine does not form fluorescent solutions.

Strychnine, $C_{21}H_{22}N_2O_2$. *Source:* Found in the seeds and bark of *Strychnos nux vomica* and other varieties of Strychnos, in company with brucine.

Properties. Colorless, fusible, four-sided, prismatic crystals; intensely bitter taste; almost insoluble in water; soluble in chloroform and dilute acids.

The *sulphate, phosphate* and *nitrate* are largely used in medicine, and are more soluble than the alkaloid. Strychnine is a most powerful poison. One-quarter grain is the minimum fatal dose.

Tests for Strychnine.

1. Dissolved in sulphuric acid, and a crystal of bichromate of potassium drawn through the solution, gives a beautiful play of colors: first blue, then violet, cherry-red, pink and yellow. This test is exceedingly delicate.

2. Precipitated by dilute solution of potassium dichromate.

Brucine, $C_{23}H_{26}N_2O_4.4H_2O$. Found with strychnine in *Strychnos. Properties.* Like strychnine—weaker physiologically. Gives red color with nitric acid.

Atropine (*Daturine*), $C_{17}H_{23}NO_3$. *Source: Atropa belladonna* and *Datura stramonium. Properties.* White, prismatic crystals; bitter; dilates pupil. Soluble in alcohol and chloroform; slightly soluble in water. Sulphate frequently used in medicine.

Tests for Atropine.

1. Dissolve in sulphuric acid, add a crystal of potassium bichromate, and a few drops of water; a green color slowly appears, and odor of orange flowers develops.

2. Action on pupil—dilates.

Hyoscyamine, $C_{17}H_{23}NO_3$. *Source: Hyoscyamus niger,* with hyoscine. Shows great resemblance to atropine in properties.

Hyoscine, $C_{17}H_{21}NO_4$, is amorphous. Used in medicine as hydrobromide, as sedative and hypnotic.

Cocaine, $C_{17}H_{21}NO_4$. *Source:* Leaves of *Erythroxylon coca* contain from .15 to .65 per cent.

Properties. Shining, prismatic crystals; slightly soluble in water, soluble in alcohol, ether and chloroform. The *hydrochloride* frequently used in medicine as a powerful local anæsthetic. When heated in sealed tube with acids it decomposes to *benzoic acid, methyl alcohol,* and *ecgonine,* $C_9H_{15}NO_3$.

Tests for Cocaine.

1. Perchloride platinum gives yellowish precipitate.

2. *Mercuric chloride* gives a white precipitate.

3. Picric acid gives a yellow precipitate.

4. Alkali carbonates and hydroxides give a white precipitate, soluble in excess of ammonia water.

Aconitine. *Source: Aconitum napellus,* contains .2 per cent. Probably a mixture of several different alkaloids.

Properties. White, or grayish white, powder; sharp, pungent taste; causes tingling sensation and numbness in the mouth and throat. A most powerful poison.

Physostigmine, Eserine, $C_{15}H_{21}N_3O_2$. *Found* in seeds of *Physostigma venenosum,* calabar bean.

Properties. Difficult to crystallize; nearly tasteless; gradually turns red. Sulphate and salicylate used in medicine, former, easily soluble; latter, only slightly souble.

Caffeine, $C_5H(CH_3)_3N_4O_2$. (*Trimethyl xanthine.*) *Source:* Coffee, tea.

Properties. Light, white, slender, long, flexible crystals; soluble in 80 parts water and 33 parts alcohol; bitter taste; neutral reaction. Citrated caffeine is more soluble, and much used in medicine.

Theobromine, $C_5H_2(CH_3)_2N_4O_2$. (*Dimethyl xanthine.*) *Source:* Seeds of Theobroma Cacao.

Properties. White crystals; slightly soluble in water, alcohol and ether; volatile at 290°; neutral in reaction, but forms salts.

PTOMAINES.

Attention was first directed to the character of the poisonous principles contained in putrefying organic matter by the Italian, Selmi, in 1876. He extracted the putrefying substances with alcohol, ether and chloroform, and thus obtained basic poisonous compounds. These he called ptomaines, or cadaveric alkaloids.

Ptomaines are feebly basic substances, containing nitrogen, formed by the action of bacteria upon nitrogenous organic matter. They have been termed animal alkaloids, but since they are formed from vegetable as well as animal substances, this term is not at all appropriate, and should be used for the class of bodies known as leucomaines.

The Formation of Ptomaines takes place as a result of the

putrefaction of nitrogenous organic matter, under the influence of moisture, suitable temperature, and presence of bacteria. The character of the ptomaine formed depends upon the kind of bacteria present, the nature of the substance decomposing, and the stage to which the decomposition has reached. The ptomaines are evidently formed by a cleavage action of bacteria upon nitrogenous material, and they represent intermediate stages of decomposition in the return of this variety of organic matter to simple inorganic forms.

The Properties of Ptomaines are much like those of the alkaloids. Some of them are liquid and volatile, others are solid non-volatile; they are basic in reaction and form crystallizable salts with acids; they are precipitated by the usual alkaloidal reagents. Ptomaines differ from alkaloids in being more easily decomposed, and for this reason they are more difficult to prepare in a pure state.

On account of this similarity in the properties of alkaloids and ptomaines, the toxicologist must be constantly on his guard in searching for poisons in putrefying bodies. Ptomaines have been found whose properties are almost duplicates of the alkaloids, atropine, conine, morphine, nicotine, strychnine, digitalin, colchicine, delphinine and veratrine. Vegetable alkaloids are said to be separable from ptomaines by precipitating from ethereal solution with oxalic acid. This is done by adding a saturated solution of oxalic acid in ether, to an equal volume of the ethereal solution of the alkaloids, and allowing to stand; the oxalates of the vegetable alkaloids will precipitate, leaving the ptomaines in solution. Cadaverine is said to be precipitated with the vegetable alkaloids. The reducing action of ptomaines upon potassium ferricyanide is made use of to distinguish them from alkaloids. If a drop or two of solution of a ptomaine be added to a solution containing ferric chloride and potassium ferricyanide, the ferricyanide is reduced to ferrocyanide and

a deep blue precipitate of prussian blue is formed. The circumstances attending the poisoning, and the symptoms of the patient, often furnish valuable aids in determining the character of the poison.

Physiological Properties of Ptomaines. A large number are found to be not poisonous, and among these may be mentioned, *methylamine, di-methylamine, tri-methylamine, ethylamine, di-ethylamine, tri-ethylamine and popylamine.*

Other ptomaines act as violent poisons, and the term toxine has been affixed to the names of such, to indicate this property. But the term *toxine* is now applied to those bacterial poisons which by absorption produce the symptoms of infectious disease.

While a number of ptomaines are violent poisons, it is now quite certain that these bodies, representing, as they do, the cleavage action of bacteria on nitrogenous matter, are not the specific factors in the causation of disease. The specific bacterial poisons are not ptomaines, but are synthetic products of bacterial life, and are properly called *toxines.*

Very little is known at present in regard to the action of the individual ptomaines on the human system. Those cases of poisoning arising from the ingestion of decomposing food, formerly known as " ptomaine poisoning," may be in part due to the presence of ptomaines, but they are now regarded as being chiefly caused by toxines, and we speak of " food poisoning," or " toxine poisoning," instead of " ptomaine poisoning." In all probability, ptomaines and toxines are synergistic in their action, and both contribute in producing the symptoms observed.

The symptoms produced by the ingestion of *poisonous mushrooms* will probably furnish a fair illustration of the action of some of the ptomaines. These symptoms have their onset in from one-half to fifteen hours. There is giddiness, nausea, salivation, vomiting, abdominal pain, dimness of vision and

dyspnœa. A period of excitement is followed by drowsiness and convulsions. The heart's action is weakened; the pulse is slow and small; the pupils are at first contracted and finally dilated. Death occurs in coma or convulsions. The antidote is atropine, which counteracts the effect of muscarine upon the heart and respiration.

Some of the poisonous ptomaines of interest are:

Tyrotoxicon. Obtained from decomposing cheese, ice cream, milk and milk products. Discovered by Professor Vaughan in 1884. It acts as a violent poison.

Muscarine. Found in poisonous mushrooms (*Agaricus muscarius*), has been made by artificial means and has been obtained from putrid fish. Acts as a violent poison, depressing the muscular tissue of the heart; action combated by atropine.

Neurine has an action similar to that of curare. It is found in decomposing animal tissues, especially putrid fish.

Typhotoxine is produced by cultures of the Eberth bacillus of typhoid fever when grown on beef-hash. This is not the specific poison of typhoid fever; the nature of the soil has much to do with the formation of this ptomaine.

Tetanine has been obtained from cultures of the tetanus germ, in an atmosphere of hydrogen, on beef broth. This ptomaine produces some, but by no means all, of the symptoms of tetanus.

Cadaverine. Found in decomposing animal bodies, especially fish. Acts as a powerful poison.

LEUCOMAINES.

The name, *leucomaine,* is derived from a Greek word signifying white. It was applied by Gautier, who was the first to make a systematic study of these bodies.

Leucomaines are nitrogenous basic substances, formed as products of tissue metabolism in the living body. They are

often called animal alkaloids, since they are usually the products of animal life.

The sources from which leucomaines are derived are the nucleins of the nuclei, and the proteids of the protoplasm of cells. They are formed during metabolism, in the tissues and cells of the body, probably by the action of enzymes or hydrolytic agents, just as ptomaines are formed by the action of bacteria upon dead proteids.

The leucomaines are not active poisons, but their retention in the animal system results injuriously, producing headache, drowsiness, dullness and a general feeling of malaise. Interference with the supply of oygen, or with the activity of the organs of elimination, results in the accumulation of leucomaines in the tissues, a condition often referred to as autointoxication.

Leucomaines are prepared from the various tissues of the body and from the excretions. The names of some of the more important ones are as follows:

Uric Acid Group of Leucomaines: Purin, Adenin, Hypoxanthine, Guanine, Methyl Guanine, Xanthine (Uric Acid).[1]

Creatinine Group of Leucomaines: Creatinine, Creatine, Crusocreatinine, Xanthocreatinine, &c.

The Poisonous Proteids, or Toxalbumins. To this class belong a number of bodies, proteid in character, represented by the venom of serpents; extractives of bacteria; and certain vegetable bodies, such as have been obtained from castor beans, and jequirity.

On account of the ease with which they decompose and their resemblance to other albumens, the toxalbumins are extremely difficult to separate, and, for this reason, very little is known in regard to their chemical character. They are among the most poisonous bodies known and are much like bacterial toxins.

[1] An oxidation product of members of this group.

Of bacterial proteids, that of diphtheria, of tetanus, and of cholera, have been obtained from cultures of bacteria of these diseases.

Very few vegetable poisonous proteids are known. Of animal proteids, we have representatives in the poison of serpents, the serum of the Conger eel, and the poison of certain insects, such as spiders, &c.

The venom of serpents, according to recent analyses, contains globulins and peptones, all of which are poisonous. This substance is an example of the most virulent of animal poisons.

TOXINES AND ANTITOXINES.

Soon after the discovery that the specific pathogenic bacteria are capable of producing basic poisonous bodies, or ptomaines, in animal bodies and in culture media, it was assumed that the symptoms of the infectious diseases were due to the presence of these bases. This view was soon abandoned, however, for it was found that filtered cultures are far more poisonous than the pure ptomaines themselves; and that after the removal of basic constituents, the filtered cultures retain their excessive poisonous properties.

These excessively poisonous bodies, which produce the symptoms of the infectious diseases, and which are formed by the action of bacteria in cultures and in the tissues of animals, are called *toxines*.

The chemical nature of toxines has not yet been determined, but they are known to be not basic, and there is not sufficient evidence to class them as ferments or albumens.

A tetanus toxine has been obtained from cultures of the tetanus germ. This toxine, when purified, proved fatal to mice in doses of .000,000,05 gm. Analysis of such a toxine by Breiger showed the following composition: Carbon, 52.8 per cent.; hydrogen, 8.1 per cent.; nitrogen, 15.7 per cent.

Further experiments indicate that toxines are not the cleavage products of bacterial action upon proteids, but that they are synthetic bodies formed as a result of bacterial life. These conclusions are justified by the fact that bacteria may be grown in culture media containing no proteids, and yet develop the poisonous toxines. This has been accomplished with the bacteria of tetanus, diphtheria, typhoid fever and some others. The toxines formed in such cases have all the virulence possessed by those grown in beef-broth.

Antitoxines are bodies formed in the animal system in response to the stimulus afforded by toxines. They serve to combat the poisonous properties of toxines, and to confer an immunity which protects the animal from further invasion by the same disease. The toxine of each infectious disease, when inoculated into the animal system, produces its own specific antitoxine.

The chemical composition and character of antitoxines is unknown. They are prepared for use in the treatment of disease, by injecting filtered cultures of bacteria, containing toxines, into an animal, in quantity insufficient to kill. These toxines stimulate the formation of antitoxine in the animal's blood. The blood of the inoculated animal is drawn off, and the sterile serum is used for treating the same disease by injecting into the human subject.

In this way, antitoxines for treating various diseases have been prepared and are being used with success. The success that has attended the treatment of diphtheria with antitoxic serum has been sufficient to repay, many times, all the pains of investigators along this line.

PROTEIDS.

Occurrence in Nature. The members of this important class of organic bodies form the chief part of the solid and fluid

constituents of the body, and are found in all the organs and tissues. They are the chief substances in which physiological changes take place, and constitute the physical basis of life.

Proteids cannot be formed by artificial means, nor are they produced within the animal body. The ultimate source from which they are all obtained is the vegetable kingdom. They are formed in the tissues of plants, from inorganic materials, under the influence of sunlight.

Composition. Nothing definite is known in regard to their molecular structure, but they all contain carbon, hydrogen, nitrogen and oxygen, and many contain sulphur and phosphorus in addition. They contain some calcium phosphate and chlorides of the alkalies, which form the ash when they are burned.

Analyses of the different proteids show the presence of the elements named in proportions which fall within the limits given in the following percentage formula:

Carbon,	50.0 to 55.0 per cent.
Hydrogen,	6.6 to 7.3 per cent.
Nitrogen,	15.0 to 19.0 per cent.
Oxygen,	19.0 to 24.0 per cent.
Sulphur,	0.3 to 2.4 per cent.

The empirical formula is represented thus:

$$C_{204}H_{322}N_{53}O_{66}S_2.$$

General Properties. The proteids are colorless, odorless, amorphous, nearly tasteless bodies. The peptones only are capable of dialysis.

All are insoluble in alcohol; some are soluble in water, others are insoluble. Some are soluble in weak saline solution, others are soluble in concentrated saline solution. All are soluble with the aid of heat in strong mineral acids, acetic acid and caustic alkalies.

The conversion of soluble proteids into an insoluble form is

known as coagulation, and may be accomplished by heat (60° or 70°), by the action of some metallic salts, or by action of mineral acids. Coagulation is a permanent chemical change in the proteid molecule.

The proteids form peptones by the action of gastric juice. They are not volatile, and they easily undergo decomposition by putrefaction. They all turn the ray of polarized light to the left.

Action of Heat upon Proteids. When heated with exclusion of air they form Dippel's oil, which contains ammonium salts of fatty acids, various amines of the fatty and aromatic hydrocarbons, and phenol, pyridine and quinoline bases.

Action of Acids and Alkalies. Boiling with strong hydrochloric or sulphuric acid produces nearly the same changes as heating with caustic alkalies. The bodies formed are chiefly ammonia, fatty acids, amido-acids, leucin, tyrosin, indol and skatol.

Strong Oxidizing Agents produce aldehydes, cyanides and fatty and aromatic acids. Nitric acid produces xanthoproteic acid, and finally, oxybenzoic acid. Chlorine forms, amongst other products, oxalic acid.

The action of putrefactive ferments is first that of peptonization (or liquefaction), and then the formation of a number of amines, amides, fatty and aromatic acids. Ammonia and hydrogen sulphide are also formed.

In the digestion of proteids, the action, in general, is to change them into proteoses and peptones, under the influence of the various digestive ferments.

General Reactions of Proteids.

Use an aqueous solution of egg albumin, 1 in 50.

1. Heated with strong nitric acid, they turn yellow, and the color deepens to orange on adding the hydroxide of ammonium, potassium or sodium.

2. *Millon's Reagent* added to the proteid gives a white precipitate which turns brick-red on heating. Millon's reagent is made by dissolving one part mercury in two parts strong nitric acid by the aid of gentle heat. The resulting solution is diluted with twice its volume of water, and the precipitate allowed to settle. The clear supernatant liquid is used as the reagent.

3. *Lieberman's Reaction.* When albumin is precipitated with alcohol and washed with ether and dried, it gives a deep-violet color when heated with hydrochloric acid.

4. To precipitate all proteids except peptones, add acetic acid to distinct acid reaction, and then a strong solution of sodium sulphate, and boil. This test is useful to separate albumin from solutions before testing for sugar.

5. To precipitate all proteids: Add tannic acid, to solutions acidulated with acetic acid; or add double iodide of mercury and potassium, with slight excess of hydrochloric acid.

6. All proteids except peptones are precipitated by ammonium sulphate solution.

7. *Biuret Reaction.* Add a few drops of dilute solution of cupric sulphate, and then an excess of solution of caustic potash; a violet color makes its appearance.

CLASSIFICATION OF PROTEIDS.

There are many systems of classification of proteids in use by different authors. It is greatly to be desired that some uniform plan shall be adopted. The following arrangement is Gray's modification of Hall's classification: it is both simple and comprehensive:

A. SIMPLE PROTEIDS:

I. Albumins.
- *a.* Egg albumin,
- *b.* Serum albumin,
- *c.* Lacto-albumin,
- *d.* Myo-albumin,
- *e.* Vegetable albumin.

II. Globulins.
- *a.* Serum globulin,
- *b.* Fibrinogen,
- *c.* Myosinogen,
- *d.* Myo-globulin,
- *e.* Globin.
- *f.* Crystallin,
- *g.* Vegetable globulin.

B. Combined Proteids:
- I. Nucleo proteids.
  - *a.* Caseinogen,
  - *b.* Vitellin,
  - *c.* Nuclein.
- II. Chromo proteids.
  - *a.* Hemoglobin,
  - *b.* Histo-hematin.

C. Derived Proteids:
- I. Albuminates.
  - *a.* Acid albumin,
  - *b.* Alkali albumin.
- II. Proteoses and Peptones.

D. Albumenoids:
- I. Native albuminoids.
  - *a.* Collagen,
  - *b.* Elastin,
  - *c.* Mucin,
  - *d.* Keratin.
- II. Derived albuminoids.
  - *a.* Gelatin.

Simple Proteids.

Albumins are soluble in water and in saturated solution of magnesium sulphate or sodium chloride, but insoluble in saturated solution of ammonium sulphate. They are coagulated by moderate heat, 63° to 75° C., and by acids and alcohol. Native albumins are: 1. *Egg albumin,* which is precipitated by ether. 2. *Serum albumin,* not precipitated by ether. This is the principal proteid constituent of the blood plasma. 3. *Lacto-albumin,* from milk. It is seen at the surface as scum when milk is boiled. 4. *Myo-albumin,* one of the proteids from muscle tissue. 5. *Vegetable albumin,* found in plants.

Globulins are insoluble in water and saturated salt solution, but soluble in dilute solution of sodium chloride. The presence of a small quantity of sodium chloride in the blood keeps them in solution. They are: 1. *Serum globulin, or paraglobulin,* a proteid of the blood plasma, and of chyle and lymph. 2. *Fibrinogen,* another proteid of the blood plasma, which differs from the foregoing in being coagulated by the fibrin ferment and calcium salts, the coagulated fibrinogen being called fibrin. It also coagulates at a lower temperature than serum albumin, and is as completely precipitated by sodium chloride as by

magnesium sulphate. 3. *Myosinogen* exists in living muscle. It coagulates after death to form myosin. 4. *Myo-globulin* is associated with myosinogen in muscle tissue. 5. *Globin* is found in the hemoglobin of the blood. 6. *Crystallin* is found in the crystalline lens of the eye.

Combined Proteids.

Nucleo Proteids are compounds of nuclein with proteids. Nuclein contains phosphorus, and hence all nucleo proteids contain this element. They generally also contain iron. They are: 1. *Casein,* or more properly *caseinogen,* the principal proteid of milk. 2. *Vitellin,* the chief proteid of the yolk of the egg. 3. *Nuclein, or cell nuclein,* the chief proteid of the nuclei of animal as well as of vegetable cells. Casein and vitellin are peculiar to certain animals.

Chromo Proteids are compounds of a proteid with an animal coloring matter. They are: 1. *Hemoglobin,* containing globin and hematin. The pigment, hematin, contains iron. 2. *Histo-hematin,* or tissue hematin, found especially in muscle.

Derived Proteids, or derived albumins. To this class are referred all proteids derived from native or combined proteids developed by physiological processes.

Albuminates are derived from native proteids by action of dilute acid or alkali. They are: 1. *Acid albumin,* formed in the stomach by the action of hydrochloric acid or other acid. *Syntonin* is a corresponding derivative of myosin. 2. *Alkali albumin,* formed by action of pancreatic juice on native proteids.

Proteoses and Peptones are derived from proteids or albuminates by hydrolysis by the process of digestion.

Albuminoids are closely related chemically to the other proteids, and are derived by processes of metabolism.

Native Albuminoids. Those existing normally are: 1.

Collagen, composing white fibrous tissue, also found in cartilage and in bone. 2. *Elastin,* composing yellow elastic tissue. 3. *Mucin,* the chief constituent of mucus, and found also in gastric juice. It has been classed as a glyco-proteid from being combined with a carbohydrate. 4. *Keratin,* the horny material of the nails, hair, skin, &c. Neurokeratin is found in the medullary sheath of nerves.

Derived Albuminoids. Of these, only one need be mentioned, *Gelatin.* It is obtained from collagen by hydration, which is accomplished by boiling with water.

PART V.

THE METHODS OF QUANTITATIVE ANALYSIS.

Qualitative analysis is analysis having for its object the determination of the character of bodies. Quantitative analysis determines the quantity of a substance.

Solution of the substance is usually the first step in analysis. If the substance be insoluble in water it may sometimes be dissolved in acidified water, or it may be rendered soluble by treatment with hydrochloric, nitric, or nitro-hydrochloric acids. When a substance has been dissolved in a strong acid for analysis, the liquid should be evaporated nearly to dryness, to remove excess of acid, and the residue dissolved in distilled water. Those bodies which cannot be made to dissolve by the aid of acids, as described, must be fused with a mixture of potassium and sodium carbonates. The resulting mass is then dissolved in distilled water.

The methods of quantitative analysis are usually of two kinds, viz.: Gravimetric and Volumetric.

The Gravimetric Method.

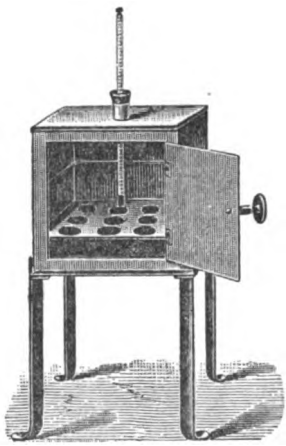
The gravimetric method of analysis consists, essentially, in the precipitation of the substance; the separation, drying, and weighing of the precipitate; the calculation of the quantity of substance from weight of precipitate.

Precipitation of the substance is accomplished by adding to the solution, in a beaker, test-tube, or other convenient vessel, the precipitating agent. The precipitating agent usually con-

sists of a body in solution which will form an insoluble definite compound with the substance which precipitates. Care should be taken to see that all the substance is thrown out of solution by the precipitant, a few drops of the latter being added after each subsidence of the precipitate until no further reaction occurs. Heating the liquid facilitates the chemical changes resulting in precipitation; it also causes an agglutination of the fine particles of some precipitates, thus facilitating their separation from the liquid by filtration.

The precipitate may be separated by decantation or filtration. Decantation consists in pouring off the supernatant liquid from a precipitate which has settled. More complete separation may be accomplished here by allowing the precipitate to drain.

FIG. 40.



Drying Oven. (After Coblentz.)

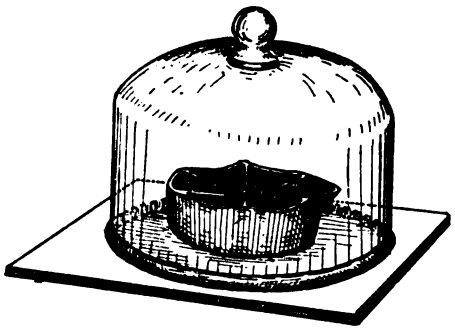
Filtration. Filters are made of various kinds of material, but they usually consist of porous paper, purified by washing with dilute hydrochloric acid. The filter is properly folded, placed in a funnel, and the mixture of liquid and precipitate poured in. By this means, two portions are obtained, viz: a filtrate, the portion running through; and a precipitate, that remaining on the filter. In order to obtain the precipitate in a pure state, it should be well washed with distilled water.

The precipitate, to be dried, may be placed with the funnel in a drying oven, and the temperature kept at 100° to 105° for a sufficient length of time to completely remove moisture.

Many precipitates require to be ignited in order to convert

them into compounds of definite composition. This is done by detaching the dried precipitate and placing it in a suitable crucible, and heating. The filter paper, containing some undetachable particles of precipitate, is burned upon the crucible lid, and its ash added to the crucible contents. The crucible and contents are then cooled over sulphuric acid in a desiccator.

FIG. 41.



Desiccator.

The weight of the precipitate is determined by weighing crucible and contents, and deducting the weight of crucible and filter ash; or the precipitate may be carefully removed to a watch glass and weighed.

The next step in analysis is to calculate the quantity of substance from the weight of precipitate. Suppose, in the above described series of experiments, we had desired to find the quantity of sulphuric acid in the original solution, and had obtained a precipitate of barium sulphate by adding barium chloride to the solution. In such a case, it would be an easy matter to calculate the quantity of sulphuric acid represented by a given quantity of $BaSO_4$, by reference to the methods of chemical calculation on page 74. Each gram of barium sulphate represents 98/233 gram of sulphuric acid.

The Volumetric Method.

The volumetric method of analysis is performed by measuring, as the name implies. It consists, essentially, in adding just enough of the reagent, to the substance tested, to produce a definite chemical reaction; and then calculating the quantity of substance from the quantity of reagent used.

The reagent for volumetric analysis is made by dissolving its molecular weight in grams (gram molecule) in one liter of distilled water at 15° C., for univalent compounds; one half this quantity for bivalent compounds; one third this quantity for trivalent compounds, &c. Such solutions are known as normal solutions, expressed thus, $\frac{N}{1}$. Deci-normal, $\frac{N}{10}$, and Centi-normal, $\frac{N}{100}$, solutions are often employed.

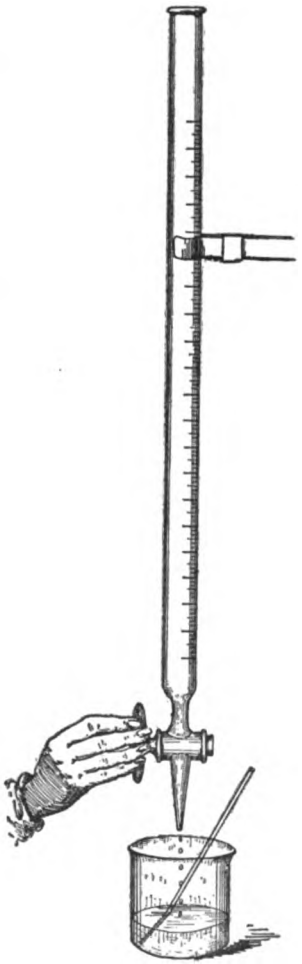
Normal solutions contain the hydrogen equivalent of the active reagent in grams per liter—Deci- and Centi-normal solutions contain the tenth or hundredth of the same equivalent. The molecular weight of caustic soda (NaOH) is 39.96; therefore the normal test solution of caustic soda is made by dissolving 39.96 gm. of this compound in water sufficient to make one liter (1000 cc.). The molecular weight of pure crystallized oxalic acid is 127.5, corresponding to the formula, $H_2C_2O_4.2H_2O$. But this compound is bivalent, containing two replaceable hydrogen atoms, and the normal test solution is made by taking one-half the molecular weight in grams, 62.85 gm., and dissolving in water to make one liter.

Each of the two solutions described is equivalent to the other—1 cc. of one being exactly neutralized by 1 cc. of the other. In the same way, all normal solutions are equivalent.

Standard Solutions are those which contain a known definite amount of reagent to be used in volumetric analysis. Such a solution may or may not be normal. Fehling's solution, the formula for which has already been given, is an example of a standard solution. It is made of such strength that 1 cc. is the equivalent of .005 gm. glucose.

In testing a substance by means of a volumetric solution, the substance is placed in a beaker, or suitable vessel, and the reagent is added, drop by drop, from a graduated burette, until the chemical change it produces is just completed. Completion of the chemical change is indicated by a change in the appearance of the mixed liquids, or by a change in color or appearance of some substance which has been added, and which is called an indicator. Phenol-phthalein is one of the bodies used as an indicator. This substance is colorless in acid or neutral media, but develops a beautiful purple-violet color when the medium becomes alkaline. If a few drops of phenol-phthalein in alcohol, be added to a solution of oxalic acid, and then caustic soda be added, drop by drop, the moment all acid is neutralized and the liquid becomes alkaline, it assumes a purple-violet color. By the use of this indicator, it is possible to tell the moment acids or alkalies are neutralized—one by the other. Various other indicators are employed, among which are—litmus, rosolic acid, methyl orange, starch mucilage, &c.

FIG. 42.



Titration.

Titration is the operation of applying the volumetric test, as described above. The expression, *titer,* is sometimes employed in the sense of standard, meaning the strength per liter or cc. of the test solution.

The methods of titration are usually of three kinds, viz.: Direct, Indirect, and Residual.

In the Direct Method the solution to be tested is acted upon by the reagent by simple contact with an equivalent quantity, as by the neutralization of an acid by a base, or vice versa.

The Indirect Method consists in the formation of a substance which liberates an equivalent quantity of another body, and by determining the quantity of the second body, the quantity of the first may be estimated. An example of this is found in testing for oxygen by heating the substance with hydrochloric acid and liberating chlorine. By determining the quantity of chlorine with potassium iodide and sodium hyposulphite, the equivalent quantity of oxygen may be estimated.

The Residual Method consists in adding a known quantity of reagent, in excess, determining the quantity which remains undecomposed, and the difference between the two represents the equivalent quantity of reagent which was consumed in the reaction. An example of this method is afforded in testing a sample of calcium carbonate, $CaCO_3$. Since it is not possible to add with any degree of accuracy the precise quantity of acid required for its neutralization, an excess of acid is added. The acid liquid is then titrated with normal alkali, by which means the quantity of undecomposed acid is determined, and this, deducted from the total quantity used, gives the amount which was consumed in neutralizing the calcium carbonate.

Calculation of Results.

In order to calculate the quantity of substance from the quantity of reagent used, reference is made to the atomic and

molecular weights of the bodies entering into the reaction. For example, if we desire to determine the quantity of hydrochloric acid in a given quantity, say 10 cc., of solution of this acid by titration with normal potassium hydroxide solution, the following equation gives the basis for the calculation, thus:

$$HCl + KOH = KCl + H_2O,$$
$$36.4 + 56 = 74.4 + 18.$$

Remembering that normal KOH solution contains the gram molecule (56 gm.) per 1000 cc., this equation shows that 1 cc. normal KOH solution requires .0364 gm. hydrochloric acid for its neutralization.

Suppose, in neutralizing the above 10 cc. of solution of HCl, 30 cc. of normal KOH solution were required. 1 cc. normal KOH requires .0364 gm. HCl for its neutralization, therefore the 10 cc. acid solution contains,

$$.0364 \times 30 = 1.0920 \text{ gm. HCl.}$$

100 cc. of the liquid would contain ten times this quantity, or 10.92 gm., or 10.92 per cent.

This example serves as an illustration of the principles involved in calculating the results of the volumetric analysis.

The following table shows more accurately a number of neutralization equivalents in grams.

One cc. Normal Acid is Equivalent to		One cc. of Normal Alkali is Equivalent to	
Ammonia	0.01701	Acetic acid	0.05986
Ammonium carbonate	0.05226	Citric acid	0.06983
Lead subacetate	0.13662	Hydrobromic acid	0.08076
Lithium carbonate	0.03693	Hydrochloric acid	0.03637
Potassium bicarbonate	0.09988	Hydriodic acid	0.12753
Potassium carbonate	0.06895	Lactic acid	0.08989
Potassium hydroxide	0.05599	Nitric acid	0.06289
Sodium bicarbonate	0.08385	Oxalic acid	0.06285
Sodium carbonate	0.05292	Sulphuric acid	0.04891
Sodium hydroxide	0.03996	Tartaric acid	0.07482

For the further study of quantitative methods the student is referred to works on chemical analysis.

PART VI.

PHYSIOLOGICAL CHEMISTRY.

INTRODUCTION.

Most of the vital activities of plants and animals are dependent upon the operation of chemical and physical, or mechanical, laws but these laws have not been sufficient, as yet, to explain all of the phenomena to be observed in the living cell.

Neither physics nor chemistry has ever been able to explain why it is that the cells of certain secretory glands, such as the mammary, are capable of removing from the blood the exact proportions of organic and inorganic constituents found in milk; or by what process the secretory cells of the glands of the stomach are capable of forming hydrochloric acid from sodium chloride, in the immediate proximity to sodium carbonate of the blood.

Certain unicellular forms of life, such as the *Vampyrella Spirogyra,* display a selective action in seeking their food which amounts almost to that of a conscious being. This minute mass of protoplasm will refuse various forms of substance until it comes to certain species of algæ, the *Spirogyra,* and, attaching itself to the cellular envelope, will dissolve this and absorb its contents.

Finding a *specific intentional activity* in this simple cell, it is equally possible that the various cells of the animal body are capable of similar conduct. We speak of the passage of nutritious material through the intestinal walls by a process of osmosis:

but the intestinal wall does not act like a dead membrane; it is lined with living cells, which by their selective action, allow certain substances to pass through into the circulation, denying entrance to others. It has been shown that the intestinal cells of cold blooded animals during the absorption of fat, send out processes to envelope the fat globule, which is then incorporated into its substance, and afterwards allowed to pass through into the lacteals.

The abandonment of the theory of "vital force" in the sense that it affects the character of the products or compounds formed by a living organism is eminently correct, but we should take pains not to apply these ideas to the activities of living protoplasm.

RELATION BETWEEN PLANT AND ANIMAL LIFE.

Physiological chemistry is the chemistry of living organisms. It embraces a study of the chemical changes taking place in the plant and animal, and the relation of these changes to vital phenomena.

The physical and chemical changes taking place in a healthy plant or animal are known as normal changes; those occurring in a diseased plant or animal are known as abnormal, or pathological. A study of the chemical changes and their products in a diseased plant or animal, is known as pathological chemistry.

Plants, under the influence of sunlight, absorb inorganic substances and build up complex unstable molecules, in which great quantities of energy are stored. These molecules furnish sources of food and energy for the animal, in whose tissues they are disintegrated and returned to inorganic forms.

The tissues of plants are made up chiefly of the elements carbon, hydrogen, oxygen, nitrogen, phosphorus, sulphur,

silicon and the metals iron, calcium, potassium, sodium and magnesium. The substances serving as plant food are taken up chiefly by the roots, which throw out an acid secretion, thus increasing the solubility of the materials with which they come in contact. The roots absorb water, carbon dioxide, nitrates, nitrites, ammonia, and the salts of the metals, besides more or less of silicon. The green parts of the plant contain chlorophyl, which under the influence of sunlight serves the function of eliminating such oxygen as is not needed, and of absorbing carbon dioxide from the air; this action, which takes place in the leaves and bark of the plant, is known as plant respiration.

The plant, in securing a supply of the elements named, obtains its carbon from carbon dioxide, its hydrogen from water, and such oxygen as is needed, from these sources also.

It obtains nitrogen from ammonia, nitrates and nitrites; sulphur from sulphates; phosphorus from phosphates; and the elements calcium, magnesium, potassium, sodium, iron and silicon from salts of these metals in the soil.

The animal receives the chief portion of its food from plant sources, either directly, or indirectly through the flesh of other animals. On the other hand, the excrementitious products of animal life furnish material for plant nutrition. Animals excrete carbon dioxide, water, urea, urates; phosphates, sulphates, and chlorides of calcium, sodium, magnesium, and potassium, while plants utilize these same products for food. The animal utilizes the oxygen given off in plant respiration, while the plant utilizes the carbon dioxide given off during animal respiration.

Thus, it is clear that a mutual adjustment between the members of the vegetable and animal kingdoms exists; the activities of plant life serving to build up food containing energy, for the animal, and the animal furnishing simple, inorganic, excrementitious material which serves as food for the plant.

CHEMICAL COMPOSITION OF THE HUMAN BODY.

Only a comparatively small number of all the elements known enter into the formation of the human body. The chief of these have been mentioned in considering the elements. The elements and the proportions in which they occur in the body are as follows:

Carbon, 13.50 per cent.; Hydrogen, 9.10 per cent.;

Oxygen, 7.2 per cent.; Nitrogen, 2.5 per cent.; Phosphorus, 1.15 per cent.;

Calcium, 1.30 per cent.; Sulphur, 0.147 per cent.;

Sodium, 0.10 per cent.; Potassium, .026 per cent.;

Chlorine, 0.085 per cent.; and the elements fluorine, iron, silicon, and magnesium in small and varying quantities.

A mere statement of the percentage of the different elements found in the body gives little idea of the real chemical composition of the different tissues and fluids. These elements are found in many different forms of combination, forming liquid and solid compounds, both organic and inorganic. By proximate analysis, these compounds have been more or less perfectly separated into what have been called proximate principles, most of which have been described under the section on descriptive chemistry.

The important organic compounds occurring in the human body are found as members of the following groups, viz., Carbohydrates, Fats and Proteids, all of which have been fully described. The inorganic constituents found are as follows, viz., water; calcium phosphate, $Ca_3(PO_4)_2$; calcium carbonate, $CaCO_3$; calcium fluoride, CaF_2; sodium chloride, NaCl; sodium phosphate, Na_2HPO_4; sodium carbonate, Na_2CO_3; sodium sulphate, Na_2SO_4; potassium chloride, KCl; potassium phosphate, K_2HPO_4; potassium carbonate, K_2CO_3; magnesium phosphate, $Mg_3(PO_4)_2$; magnesium carbonate, $MgCO_3$; iron, in hemoglobin of the blood and traces in other tissues and fluids.

A number of other compounds are found, most of which probably represent different stages of tissue consumption or retrograde metamorphosis. They are: acetic, lactic, oxalic, butyric and propionic acids; urea, uric acid, xanthin, hippuric acid, creatin, creatinin, &c.; alcohol, glycerin, cholesterin; and certain pigments, as those found in urine and bile.

Animal Food. The energy manifested in the various activities of the animal organism results in the disintegration or consumption of the living tissue cells. In consequence of this disintegration, materials have to be constantly supplied for the restoration and maintenance of cellular integrity. *Foods* are substances which when taken into the animal body yield energy by their own disintegration, furnish constructive material to cells, or prevent cellular consumption.

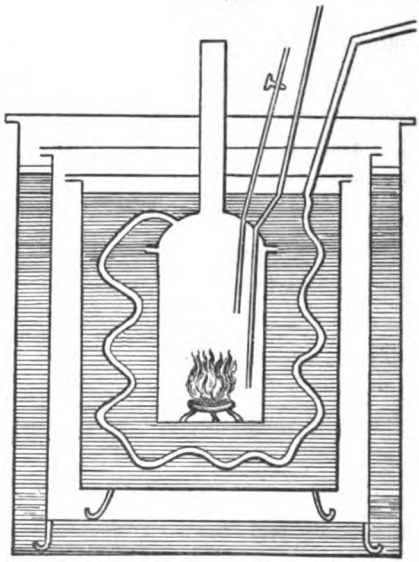
The substances used as foods contain compounds corresponding to those found in the body. These compounds are of four kinds, viz.: Proteids, carbohydrates, fats, and inorganic salts, including water. The compounds themselves are known as food principles, in contra-distinction to the crude articles of diet.

The animal body is thus seen to be a kind of machine, capable of self-restoration and regulation within certain limits. It takes up compounds of complex molecular structure found in the crude articles of diet, and by their gradual oxidation and disintegration it utilizes the store of energy which they contain. This energy is manifested in heat, muscular activity, mental activity, and the various other forms of motion of which the body is capable.

The value of a substance for food is measured by the amount of energy it is capable of producing. This is generally expressed in heat units, or calories. The heat producing value of a given article of food is determined by means of the calorimeter. Fats and carbohydrates produce the same amount of

heat when burned in the calorimeter as when consumed in the animal body. In the case of proteids, the quantity is greater, because proteids are only oxidized to the extent of urea in animals; but the difference is known to be 2.523 calories, which is the number of heat units produced by burning urea. The

FIG. 43.



Calorimeter.

number of kilogram calories,[1] when this difference is accounted for, is about the same for carbohydrates and proteids when consumed in the animal body. The heat value of the three important energy-producing foods in kilogram calories is shown to be as follows:

1 gram proteid or carbohydrate yields..... 4.120 calories.
1 gram fat yields..... 9.353 calories.

[1] The kilogram calorie is the quantity of heat required to raise the temperature of 1 kilogram of water from 0° to 1° C.

The Utilization of Food. *The proteids* of the food, after undergoing digestion and conversion into peptones, pass into the blood stream in the form of proteids characteristic of the blood, and are carried to the tissues where they enter, in part or entirely, into the structure of the protoplasm of tissue cells.

In the process of metabolism, the proteids become oxidized and undergo disintegration. They are converted into a compound containing carbon, probably a carbohydrate, and into other compounds containing nitrogen. The nitrogenous end product of proteid metabolism is urea, and the probable antecedents to the formation of urea are creatin, glycocol, sarcolactic acid, ammonium lactate, ammonium carbonate and ammonium carbamate. The disintegration of the proteid molecule is attended by the liberation of energy.

The Fats after digestion pass into the lymphatic vessels and through the thoracic duct into the circulation. They rapidly disappear from the circulation, and are believed to supply body fat in part, but the larger portion is directly oxidized into carbon dioxide and water, setting free the large quantity of molecular energy which they contain. The fat of the tissues is partly supplied in the disintegration of the proteid and carbohydrate molecule.

The Carbohydrates are converted into dextrose by digestion and pass into the circulation as such. A large portion is stored in the liver and muscles as glycogen; a large portion is at once oxidized, liberating its molecular energy; a portion contributes to the formation of fat.

The inorganic food principles, though used in smaller amount than the organic, are equally necessary for the maintenance of physiological activities.

Water is absorbed directly into the circulation after its ingestion. Its presence in all the fluids and tissues of the body is necessary in order that they may perform their functions.

It serves to dissolve the food principles and to carry them in the blood and lymph stream to the body tissues. It serves to dissolve the waste products of metabolism, and to remove them, by its elimination through the various excretory glands.

Sodium Chloride is taken into the body with the food, both as a constituent of the usual food-stuffs and as a condiment. By its presence it facilitates the solution of various body principles, it facilitates cellular activity, and it is believed to furnish the chief material from which hydrochloric acid of gastric juice is formed.

Potassium Phosphate and Carbonate and the corresponding salts of sodium furnish a mild degree of alkalinity to the blood and lymph, a condition necessary to the activity of tissue cells.

Of Calcium Salts, the phosphate and carbonate are utilized in the structure of bones and teeth, and the phosphate is found in the nervous tissues. The absence of the salts of calcium from the food of young animals produces a condition similar to that seen in rickets.

Iron is taken into the animal from organic and inorganic sources, and it enters into the composition of the hemoglobin of the blood: it is also found in traces in other tissues, and it is eliminated chiefly by the feces.

Vegetable Acids serve to increase the secretion of the digestive fluids, and, entering the circulation as salts, they increase elimination through the kidneys. Entire absence of vegetable acids from the diet results in the development of scurvy, while an excessive quantity gives flatulence and diarrhea.

The Supplementary Foods, coffee, tea and cocoa, act as stimulants to the nervous system and heart, relieving the sense of fatigue following mental or physical exertion, and increasing the power of continuous mental effort, but they have no influence over proteid metabolism. These supplementary foods depend upon the presence of the alkaloids, caffeine, theine, and

theobromine for their stimulating and sustaining properties. Tea contains a large percentage of tannic acid which is liable to act as an irritant to the digestive organs when this beverage is taken in large amount. Cocoa has a certain nutritive value not possessed by the others on account of the fat and proteid which it contains.

Alcohol, when taken in small amount, acts as a stimulant to the digestive organs. It increases the heart's action and dilates the arterioles, producing a sense of warmth, but it increases heat elimination. It produces excitation of the brain. In large quantities alcohol acts as a paralyzant, and deranges the organs of digestion. The long-continued use of alcohol, even in moderate amount, is liable to derange the digestive organs by its irritant action upon the mucous membrane, and give rise to digestive disturbances. In excessive quantities it produces muscular weakness, lessened mental power, depression of temperature, and structural changes in the liver, kidneys, brain, spinal cord and other organs of the body.

Alcohol is oxidized in the tissues, and thus temporarily contributes to bodily energy, but experimental evidence does not show conclusively that it has any value as an article of food. The relation of alcohol to proteid metabolism is still a matter of experimental investigation, however, and the question of its value as an article of food has not been satisfactorily determined.

The Blood is a highly complex fluid, and as found in the animal body it is of two kinds, viz., arterial, or oxidized blood, having a bright red color; and venous, or deoxidized blood, whose color is of a darker hue.

Blood is an opaque liquid; it has a peculiar odor, which is augmented by the addition of sulphuric acid; its reaction is alkaline, due to the presence of disodium phosphate and sodium carbonate; its specific gravity averages 1.056 in the male, and

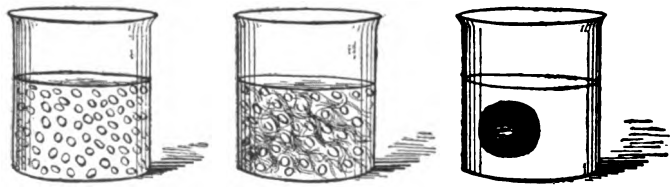
1.053 in the female. The temperature of the blood in health varies from 98.2° F., in the superior vena cava, to 103.4° F. in the hepatic vein.

The microscope reveals the fact that blood is made up of a fluid portion, called plasma, and of certain minute solid bodies floating in the plasma, known as corpuscles.

A few minutes after blood is drawn from the animal, about five to seven minutes in the human subject, it undergoes a change which results in its conversion into a semisolid, gelatinous mass. This change is known as coagulation. A microscopic examination of coagulated blood shows the presence of a network of fine fibrils extending in all directions through its substance, having the corpuscles entangled in its meshes. These fibrils consist of fibrin. Fibrin may be obtained free from other substance by stirring the blood, as it coagulates, with a bundle of small glass rods to which the fibrin adheres, and then washing with pure water in order to remove the blood corpuscles.

Fibrin is a form of proteid which is produced by coagulation of the fibrinogen of blood plasma under the influence of

FIG. 44.



Coagulating Blood.

the fibrin ferment in the presence of calcium salts, when blood is drawn from the body. The exact chemical changes taking place in coagulation of the blood are not known at the present time.

When coagulated blood is allowed to stand for a time a clear, straw colored fluid, called blood serum, makes its appearance on the surface of the clot. Upon further standing, the fibrin contracts into a smaller mass, with separation of serum, until finally it forms, with the enclosed corpuscles, a red clot which floats indifferently in the surrounding serum.

If blood be prevented from coagulating by the addition of magnesium sulphate (1 volume of a 25 per cent. solution to three volumes of blood), or by other suitable means, the corpuscular portion settles to the bottom of the vessel, forming a layer somewhat less than one-half the total volume. The supernatant, or fluid portion, constitutes the plasma.

Plasma is a transparent, pale yellow, slightly viscid liquid; having a specific gravity of 1.026 to 1.029. It is composed of water, proteids, sugar, fatty matter, urea, cholesterin, lecithin, and the inorganic salts, sodium chloride, potassium chloride, potassium sulphate, sodium phosphate, sodium carbonate, calcium phosphate and magnesium phosphate.

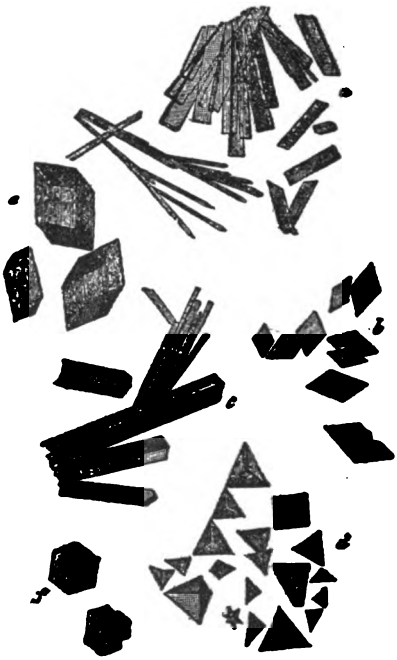
The proteids of plasma are serum-albumen, paraglobulin and fibrinogen. The last named is converted into fibrin during coagulation.

The Blood Corpuscles are of three kinds, viz., Erythrocytes, or red blood cells; Leucocytes, or white blood cells; Blood plaques, or blood plates.

The Red Corpuscle is non-nucleated; its shape is that of a circular, flattened, biconcave disk; when viewed under the microscope it has a yellowish color; its transverse diameter is .0075 mm.; its thickness is .0019 mm.; it is a structureless mass of protoplasm, containing hemoglobin, which can be dissolved out with distilled water. Besides hemoglobin, the blood corpuscle contains a proteid, lecithin, cholesterin, potassium phosphate and other inorganic salts in minute amount.

The Amount of Hemoglobin present in the blood corpuscle is estimated to be 90 per cent.; this is in the amorphous condition and combined with the protoplasm of the cell. By treating the corpuscles with distilled water and slowly evaporating,

FIG. 45.



Hemoglobin Crystals. (Brubaker.) *a-b*, human; *c*, cat; *d*, guinea pig; *e*, hamster; *f*, squirrel.

the hemoglobin may be obtained in the form of rhombic, prismatic crystals, of red color. Hemoglobin contains from .4 to .6 per cent. of iron; it has a strong affinity for oxygen, which, however, it readily gives up to other bodies. Hemoglobin serves as the oxygen-carrying substance of the blood. *Oxy-hemoglobin* is the oxidized variety, found in arterial

blood; *reduced hemoglobin* is found in venous blood. *Methemoglobin* is a modified form of hemoglobin, found in certain fluids, such as cystic fluids, and blood transudates.

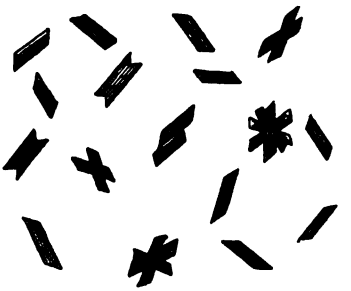
The chemical analysis of hemoglobin freed from water of crystallization by drying at 100°, shows a probable formula of, $C_{600}H_{960}N_{154}O_{179}S_3Fe$, with the immense molecular weight of 13,332.

Hematin. Oxy-hemoglobin is decomposed by action of acids or alkalies into globulins, and a colored compound containing iron, known as *hematin.* Hematin constitutes 4 per cent. of hemoglobin, and, when pure, is a metallic-looking powder, bluish-black in color. Two varieties of this compound are known, one formed by action of acids, and the other by action of alkalies, on hemoglobin.

Hemochromagen is a pigment, formed by decomposition of hemoglobin in absence of oxygen. Its solution absorbs oxygen, and is converted into hematin.

Hemin. Hematin unites with hydrochloric acid to form *hematin hydrochlorate, or hemin,* which produces microscopic crystals, in rhombic plates. The formation of these crystals serves as a test for blood. Hemin crystals may be obtained from a dry blood smear on a microscope slide by adding a minute fragment of sodium chloride, a drop of distilled water and gently warming. A cover glass is then placed over the smear, and a drop of glacial acetic acid allowed to flow in from the side. Hemin crystals are then observed under the microscope.

FIG. 46.



Hemin Crystals.

Leucocytes, or White Corpuscles. The proportion of white

to red corpuscles is about 1 of the former to 700 of the latter. The white corpuscle is grayish in color, globular or irregular in shape, and consists of a mass of protoplasm containing granules and a nucleus. Its size is about .0011 mm., or 1/2500 inch, in diameter.

The white corpuscles consist of 90 per cent. of water. The solid portion is made up of nuclein, nucleo-albumin, cell globulin, lecithin, fat, glycogen, alkaline and earthy phosphates. The quantity of phosphorus which they contain is relatively large.

Blood Plaques are grayish-white disks of protoplasm floating in the blood stream. Their function is unknown.

Lymph is the liquid obtained from the lymphatic vessels. It is a colorless, slightly alkaline liquid, having a specific gravity of about 1.030. Lymph contains a large number of white corpuscles, and it coagulates when drawn from the vessels. Lymph is composed of serum-albumin, fibrinogen, fat, sugar and inorganic salts.

Muscle. The chemical composition of living muscle is a matter which has not been accurately determined, because chemical changes take place in its constituents soor after death and because some of the muscle constituents undergo decomposition in the process of analysis. According to Halliburton, muscle contains water, proteids including pigment, gelatin, fat, extractives and inorganic salts.

If fresh muscle tissue be freed from blood, fat and connective tissue, frozen, and rubbed in a mortar, a slightly alkaline, or neutral, yellowish liquid can be expressed, which is called muscle plasma. Muscle plasma undergoes coagulation, yielding myosin and muscle serum. This change takes place in the muscle soon after death, resulting in *rigor mortis*. From muscle serum the proteids, myo-globulin and myo-albumin may be obtained. From muscle plasma the proteids, paramyosinogen and myosinogen may be obtained; myosinogen is

converted into myosin in muscle coagulation, but both of these proteids enter into the formation of muscle clot. A coagulating enzyme, known as myosin ferment, is found in muscle plasma.

The extractives of muscle are, creatin, creatinin, xanthin, carnine, urea, uric acid, carnic acid, glycogen, dextrose, inosite, fat and lactic acid. The inorganic salts are chiefly phosphates of potassium, and small quantities of sodium bicarbonate; salts of calcium, iron and magnesium.

Bone contains a large percentage of inorganic constituents. In dried bone the inorganic matter amounts to 69 per cent. In children the percentage of organic matter is greater than in adults, and, as a result, the bones of the former are less liable to fracture.

The inorganic constituents of bone are, tricalcium phosphate, magnesium phosphate, calcium carbonate, calcium fluoride, soluble salts and traces of iron.

The proteid constituent of bone is ossein, which yields gelatine when boiled with dilute hydrochloric acid.

Teeth contain the largest percentage of inorganic matter of all body tissues, the enamel being the most dense.

The dentine forms the chief mass of the tooth, being covered by enamel at the crown and neck, and covered by cement at the fang. Cement has nearly the same composition as bone. Dentine contains, in woman, 72.39 per cent. of inorganic matter; in man, 79.00 per cent. of inorganic matter.

Enamel is an exceedingly dense substance, having the following composition: Water and organic matter, 3.6 per cent.; calcium phosphate and calcium fluoride, 86.9 per cent.; magnesium phosphate, 1.5 per cent.; calcium carbonate, 8.0 per cent.

Tartar is a substance which deposits on the teeth from the alkaline saliva. It consists of calcium phosphate, calcium carbonate, organic matter and bacteria.

Hair, Nails, Feathers, Horns, Hoofs, etc., are made up of cholesterine and bodies containing nitrogen, called keratins. The keratins are probably mixtures of compounds.

DIGESTION.

The term, digestion, refers to the physical and chemical changes which take place in food in the alimentary canal in health. These changes begin in the mouth and they continue, with varying degree of intensity, throughout the entire length of the food canal.

The process of digestion is directed to the solution of nutritive principles of food, to its conversion into absorbable forms, to its separation from insoluble and worthless constituents, and to the extrusion of the latter from the body. The study of the process is divided into mouth, stomach and intestinal digestion; though the three processes are closely related and inter-dependent.

In Mouth Digestion the food undergoes mechanical division, and it is thoroughly mixed with saliva by the action of the teeth and tongue. The action of saliva is to begin the digestion of starchy foods, partly converting them into sugar.

Saliva is the active digestive fluid of the mouth; it is the mixed secretion of the parotid, submaxillary and sublingual glands. Saliva is a viscid, opalescent, frothy liquid; its reaction is usually alkaline, though it may be neutral or acid from fermentation of food particles, or in disease; its specific gravity is 1.003 to 1.006. In composition, saliva consists of 99.5 parts water, and the solid portion is made up of epithelium, soluble organic matter, potassium sulphocyanate and inorganic salts.

The soluble organic matter is made up of mucin, globulin and serum albumin. The inorganic constituents, besides potassium sulphocyanate, are calcium, sodium and magnesium phosphates, sodium chloride and carbonate and potassium chloride.

The daily quantity of saliva is estimated to be 1305 grams, or 2.8 pounds.

Ptyalin is the digestive ferment of saliva, and it occurs as a part of the soluble organic constituents. It is present in all animals except those which are purely carnivorous; its action is to convert starch into sugar, which can be easily shown by adding saliva to mucilage of starch, keeping the temperature at 40° C., and then testing the liquid.

Ptyalin acts best in a weak alkaline solution, though its action is not arrested by a weak acid solution. The activity of ptyalin is destroyed by the presence of strong acids or alkalies.

The changes which occur in the conversion of starch into sugar by ptyalin consist in the addition of water, or hydrolysis. Soluble starch is first formed, and this is converted into erythrodextrin and maltose; erythrodextrin is further converted into acroodextrin and maltose. Erythrodextrin gives a red color with iodine; acroodextrin gives no color.

Stomach Digestion. The food passes from the mouth, through the esophagus, into the stomach. Salivary digestion of starches continues for about twenty minutes to half-an-hour, until the alkaline saliva is neutralized and considerable free hydrochloric acid is formed.

In the stomach the food is converted into a turbid liquid, called chyme, by the action of gastric juice and the muscular movements of this organ, aided by such fluids as have been ingested.

Absorption through the stomach walls takes place only to a limited extent, being confined chiefly to the water, inorganic salts and sugar.

Gastric Juice is the digestive fluid of the stomach. It is secreted, as a result of the mechanical and chemical stimulus of substances introduced as food, by glands situated in the stom-

ach walls. A strong desire for food, or certain reflex nervous impulses, such as those produced by pleasant odors of prepared food, are said to stimulate secretion of gastric juice: strong emotion, as fear, anger, or grief, diminish the secretion.

Gastric juice is a clear, colorless, acid liquid; its specific gravity is 1.002 to 1.005; it has a saline and acid taste; it resists putrefaction and acts as an antiseptic. Gastric juice contains water, organic matter, hydrochloric acid; calcium, sodium, and potassium chlorides; calcium, magnesium and ferric phosphates. The organic matter is made up of mucin, a proteid, pepsin and rennin, or pexin. Pepsin and pexin are formed by action of hydrochloric acid upon pepsinogen and pexinogen, zymogen bodies formed by the secretory cells. Hydrochloric is the normal acid of the stomach, though gastric juice frequently contains lactic and acetic acids, which are believed to be due to fermentation. The quantity of hydrochloric acid varies, but it occurs to the extent of .1 to .4 per cent.

The action of gastric juice on ingested foods is that of an antiseptic, preventing putrefaction; and that of a digestant, converting proteids into peptones.

The digestion of proteids is a progressive form of chemical change, resulting first in the formation of acid albumen, which is split into the primary proteoses, proto-albumose and hetero-albumose. These primary proteoses are further changed into secondary proteoses, consisting of two corresponding deutero-albumoses, which in turn are converted into two corresponding peptones called hemi-peptone and anti-peptone—sometimes designated ampho-peptones. These changes are believed to be due to the action of pepsin upon acid albumen.

Rennin (*or pexin*), is the milk-curdling ferment of the gastric juice.

The product of stomach digestion, called chyme, passes through the pyloric orifice into the duodenum. This transfer takes place in small portions at a time, until the stomach is emptied of its contents.

Chyme is acid in reaction; it consists of water, inorganic salts, acidified proteids, hemi-peptone, anti-peptone, carbohydrates, liquefied fats, and indigestible portions of food. This acid liquid is neutralized by the alkaline intestinal secretions, and some of its contents are precipitated. When this occurs, stomach digestion ceases and intestinal digestion begins.

Examination of Stomach Contents, To obtain a specimen for examination a test meal is given, on an empty stomach, of a few ounces of bread and a cup of water or weak unsweetened tea. After the lapse of an hour, the contents of the stomach are withdrawn with the stomach-tube, and filtered. If the fluid is too thick, it may be diluted with a definite quantity of water.

The examination consists of a determination of reaction, of free acids, of free hydrochloric acid, of lactic acid, of pepsine, rennin, proteids, carbohydrates; estimation of total acidity, of free acids, of free hydrochloric acid, of combined hydrochloric acid, of total organic acids.

1. *Reaction* is determined by use of litmus-paper, and in the normal secretion it should always be acid.

2. *Detection of Free Acids* may be accomplished by use of congo-red paper. A drop of the fluid placed on a piece of this paper produces a blue color if free acids are present.

3. *Free Hydrochloric Acid* may be recognized by a number of tests:

(*a*) Methyl-violet in strong aqueous solution, added to the gastric juice, produces a change of violet to blue in presence of free HCl.

(*b*) Resorcin solution, obtained by dissolving 5 parts resorcin, 3 parts cane sugar, in 100 of diluted alcohol, gives a bright red color in presence of hydrochloric acid when warmed. The test is applied by adding 5 drops resorcin solution to an equal quantity of gastric juice and warming gently; as the liquids evaporate, a bright red color appears.

(*c*) Dimethyl-amido-azobenzol in .5 per cent. solution in alcohol, mixed with the gastric juice, gives a cherry-red color. This test is so sensitive as to show so little as .002 per cent. hydrochloric acid.

4. *Lactic Acid* may be recognized by mixing 2 c.c. Uffelmann's reagent with 2 c.c. of the gastric juice; in the presence of lactic acid it gives a yellow color.

Since the presence of other bodies sometimes interferes with this reaction, it is well to extract 10 c.c. of gastric juice with 50 c.c. of ether, evaporate the ethereal solution (which contains the lactic acid) to dryness, add a few drops of water to the residue, and then apply the test.

Uffelmann's reagent is prepared by adding two drops ferric chloride solution to 10 c.c. of one per cent. carbolic acid solution, and diluting with water to a pale blue color.

5. *Pepsin* in presence of free hydrochloric acid may be recognized by its power to digest dried fibrine. Ten c.c. of the gastric juice is placed in a test-tube, the fibrin added, and the temperature kept at 40° C.; in presence of pepsin the fibrin rapidly dissolves.

6. *Rennin* may be recognized by neutralizing 10 c.c. of gastric juice with N/10 potassium hydroxide solution, and mixing with 10 c.c. fresh milk. The mixture kept at 40° C. should form a coagulum in fifteen minutes if rennin be present.

7. *The proteids* likely to be found in gastric juice are syntonin, albumoses and peptone.

Syntonin precipitates when the gastric juice is neutralized; the precipitate is soluble in acids or alkalies.

Albumoses are precipitated by saturated solution of ammonium sulphate.

Peptones may be recognized by making the gastric juice strongly alkaline with potassium hydroxide and adding a few drops of solution of cupric sulphate (1 to 1,000). With this solution peptones produce a red color.

8. *Starch* may be recognized by the blue color it gives with iodine solution. The same reagent gives a brownish-red color with erythrodextrin, and has no effect upon acroodextrin.

Quantitative Tests.

1. *Estimation of Total Acidity* may be accomplished by adding a few drops of phenolphthalein solution to 10 c.c. of the filtered gastric juice, and titrating with N/10 sodium hydroxide solution.

The results are expressed in the percentage of c.c. sodium hydroxide used, thus: Forty per cent. acidity indicates that 40 c.c. N/10 NaOH are required to neutralize 100 c.c. of gastric juice. One c.c. N/10 NaOH neutralizes .00365 gm. hydrochloric acid. If 4 c.c. N/10 NaOH be required to neutralize 10 c.c. gastric juice, it would correspond to 4 times .00365 hydrochloric acid, or .01456 gm. hydrochloric acid in 10 c.c. of the solution tested, or 0.146 per cent.

2. *The Total Quantity of Free Acids* may be estimated by adding congo-red as an indicator and titrating 10 c.c. gastric juice with N/10 sodium hydroxide until a blue color is produced. Congo-red is unaffected by acid salts, and thus shows the quantity of free acids only.

3. *Free Hydrochloric Acid* may be determined by adding 5 drops dimethyl-amido-benzol solution (solution to be made as above described) to 10 c.c. of gastric juice, as an indicator, and titrating with N/10 sodium hydroxide solution: disappearance of the red color indicates end of the reaction. By deducting the quantity of free hydrochloric acid from the quantity of total free acids, the quantity of free organic acids is determined.

4. *Combined Hydrochloric Acid* may be estimated by first titrating 10 c.c. gastric juice, using 3 drops 1 per cent. solution alizarine as an indicator, with N/10 sodium hydroxide solution: a violet color indicates end of the reaction. The acidity

determined here is due to free hydrochloric acid, acid salts and organic acids; the difference between this and the total acidity indicates the quantity of combined hydrochloric acid.

5. Difference between the estimated quantity of combined hydrochloric acid and free hydrochloric acid shows acidity due to organic acids and acid salts.

Intestinal Digestion. The intestinal fluids are alkaline in reaction and are made up of the pancreatic juice, intestinal juice and bile.

The pancreatic gland produces two secretions: one is an internal secretion, and passes directly into the blood to regulate the assimilation of carbohydrates; the other, the pancreatic juice, passes into the intestine to take part in digestion.

Pancreatic Juice is a slightly opaque, viscid, alkaline liquid; it contains about 5 per cent. of solids, two thirds of which are organic in character. Of the inorganic salts, sodium carbonate is the most important constituent.

Among the organic constituents of pancreatic juice, a number of ferments are found; these are: Amylopsin, which converts starch into sugar; Trypsin, which converts proteids into peptone, in alkaline solution; Steapsin, which decomposes fats into fatty acids and glycerin, and which emulsifies fats; and a milk-curdling ferment.

On account of the presence of so many different ferments, the pancreatic juice is capable of a more extended digestive action than any of the other alimentary fluids. It acts upon carbohydrates, fats and proteids.

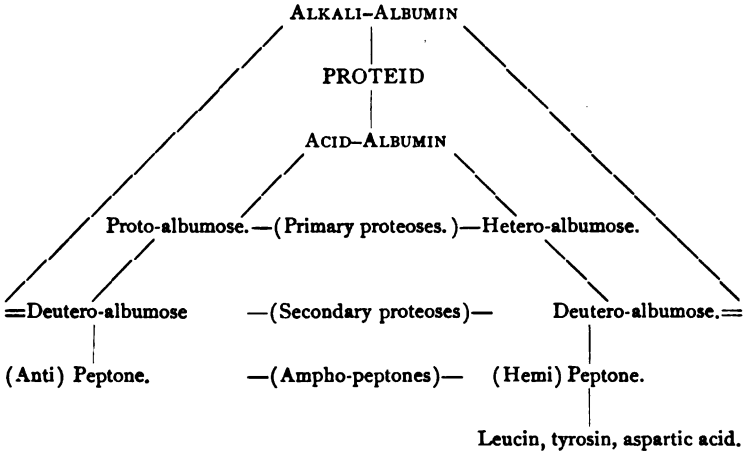
Starch is converted into maltose and dextrose, by the ferment amylopsin, passing through the intermediate stages of dextrin formation, similar to those of salivary digestion. The action of amylopsin is much more energetic than that of ptyalin.

Fats are decomposed by the ferment steapsin, with forma-

tion of fatty acids and glycerine. The liberated fatty acids form soaps with sodium carbonate of the pancreatic juice, and also with cholesterin of the bile. This mixture of compounds serves to aid in the emulsification of undecomposed fats.

Proteids are converted into peptones by aid of the ferment trypsin. The first change taking place in proteids is the formation of alkali-albumen, and the end products are, peptone, leucin, tyrosin and aspartic acid. The intermediate stages of the conversion have not been accurately determined, but it is believed that the alkali-albumen is converted into deutero-proteoses, and this into peptone. Since half of the peptone is decomposed by further digestion into leucin, tyrosin and aspartic acid, and the other half remains unchanged, the peptone is thought to be of two kinds, which are called anti-peptone and hemi-peptone. This corresponds to two forms of secondary proteoses (deutero-proteose) as found in stomach digestion.

Primary proteoses (proto-albumose and hetero-albumose) are not found as a result of pancreatic digestion. Proteid digestion begins in the stomach and is finished in the intestine.



Diagrammatic illustration of gastric and pancreatic digestion of proteids.

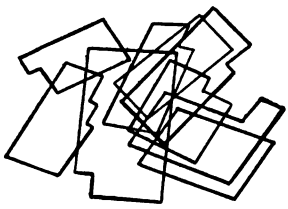
Intestinal Juice, secreted by the intestinal glands, takes a part in digestion of which very little is known. Experiments indicate that it serves to complete the conversion of carbohydrates into glucose and levulose, by action of a ferment called invertin.

Bile is secreted by the liver cells. It is poured into the intestine along with the pancreatic juice, and aids the process of digestion, particularly in the emulsification and absorption of fats.

Bile is a green or golden-yellow, somewhat viscid liquid; its reaction is alkaline; its specific gravity is from 1.010 to 1.020; it has a bitter taste. The daily quantity is said to be 1000 to 1700 c.c., most of which is reabsorbed from the intestinal walls. Bile contains from 7 to 20 per cent. of solids, as follows: Sodium glycocholate and sodium taurocholate, fats, soaps, cholesterin, mucus, pigment, lecithin.

The Normal Bile Pigments are bilirubin and biliverdin; they impart a green and red color, respectively. Bilirubin is formed from hematin of the red coloring matter of the blood. Hematin combines with water and looses its iron, in the liver, forming bilirubin. Bilirubin undergoes oxidation in the gall-bladder, forming biliverdin.

FIG. 47.



Cholesterin Crystals.

Cholesterin, $C_{27}H_{45}OH$, has the structure of an alcohol, but on account of its greasy character and solubility in ether, it has been classed as a fat. Cholesterin is always found in bile, but it occurs in the blood, brain, nervous tissues and other parts of the body. It is found, also, in the vegetable kingdom. Cholesterin occurs in transparent, thin, rectangular crystals; it is held in solution in the bile by presence of the bile salts; when

these are deficient, it sometimes deposits in the gall-bladder, forming gall-stones, which are more or less colored by altered bile pigments. Cholesterin is discharged from the body as stercorin in the feces.

Sodium Glycocholate and Sodium Taurocholate are compounds formed by replacement of hydrogen in glycocholic acid, $C_{26}H_{43}NO_6$, and taurocholic acid, $C_{26}H_{45}NO_7S$, with sodium.

Glycocholic Acid may be decomposed into glycocol, or amido-acetic acid, $CH_2NH_2CO_2H$, and cholic acid, $C_{24}H_{40}O_2$.

Taurocholic Acid decomposes into taurine, or amido-ethyl-sulphonic acid, $C_2H_4NH_2HSO_3$, and cholic acid. These decompositions are effected by heating with dilute acids or alkalies; they also occur in the intestines.

The Fermentative and Putrefactive Changes taking place in the intestines result in the formation of lactic acid, butyric acid, carbon dioxide and hydrogen, from fats; valerianic acid, ammonia and carbon dioxide, from leucin; indol from tyrosin, antecedent to indican of the urine. Skatol is also formed from proteids and gives rise to the odor of feces, along with other substances, such as hydrogen sulphide and organic acids.

Fecal Matter consists of the indigestible portions of food, the useless products of digestion, epithelium, residuum of intestinal juices and excretions from the blood. The normal daily quantity varies from four to six ounces.

RESPIRATION.

Respiration is the act which furnishes a supply of oxygen to the tissues and removes carbon dioxide. The consumption of oxygen and formation of carbon dioxide in the tissues is called internal respiration, and it takes place as a part of tissue metabolism. Oxygen is carried in arterial blood from the lungs to the tissues, and carbon dioxide is returned in venous blood from the tissues to the lungs. In the lungs, an

exchange of gases between the blood and inspired air takes place, which is called external respiration.

The changes taking place in the composition of respired air consequently relate to the quantities of oxygen and carbon dioxide. Inspired air contains, by volume, 20.8 per cent. of oxygen; 79.2 per cent. of nitrogen; traces of carbon dioxide (.04 per cent.); and a variable quantity of watery vapor. Expired air contains, 16.02 per cent. of oxygen; 79.6 per cent. of nitrogen; 4.38 per cent. of carbon dioxide; watery vapor to saturation, and organic matter. The quantity of oxygen lost amounts to 4.78 per cent., and the quantity of carbon dioxide gained amounts to 4.38 per cent. The gain in organic matter is variable, and the same may be said of watery vapor, the latter depending upon variations in the temperature of respired air.

The oxygen of respired air enters into the alveoli of the lungs, during respiration, and is taken up by the blood circulating in capillary vessels surrounding the alveoli. In the blood the larger portion of oxygen is in combination with hemoglobin, though a small portion is also contained in the blood plasma. Oxy-hemoglobin imparts the bright red color to arterial blood, and gives up its oxygen in passing through the capillary vessels of the tissues. Reduced hemoglobin passes into the veins, from the capillaries of the tissues, and imparts the dark red color to venous blood.

Carbon dioxide exists in the blood partly dissolved and partly combined with the salts of the plasma. It is derived from the tissues of the body as the blood-stream passes through in capillary vessels, and it is carried to the lungs in the returning venous blood. Carbon dioxide is eliminated from the blood into the alveoli of the lungs and passes out as a constituent of expired air.

MILK.

Milk is the secretion of the mammary gland of the female, intended for the nutrition of the nursing mammal. It contains all the food principles, both organic and inorganic, in proper proportion for the sustenance and development of the young animal for a limited period of its life. The composition of milk consequently varies in different animals, in regard to the relative proportion of its constituents, according to the needs of the species; it also varies in the same animal under varying conditions of food and health.

Cow's milk, a typical milk, is of interest because it is so largely used as an article of food; human milk is of interest on account of its relation to the nutrition of the infant.

A number of analyses of cow's milk and human milk show an average composition, as follows:

	Cow's Milk.	Human Milk.
Water	86.70	88.30
Proteids (casein and albumin)	4.40	2.00
Fat	3.65	3.40
Milk sugar	4.50	6.00
Inorganic salts	0.75	0.30

In addition to the above inorganic constituents, milk contains a number of extractives in very small amount, viz.: Lecithin, creatin, urea, citric acid and phospho-carnic acid.

The gases of milk are, carbon dioxide, 7.06 per cent.; oxygen, 0.1 per cent.; nitrogen, 0.7 per cent., by volume.

Milk is an opaque, white liquid. The inorganic salts, proteids and lactose are in solution. The fat is in suspension in the form of small globules, having a diameter varying from .0015 mm. to .005 mm., in a condition in which they do not spontaneously coalesce. The properties of fat-globules indicate that they have a fluid proteid envelope. The specific gravity of normal milk varies from 1.028 to 1.035; its reaction

in herbivorous animals and the human subject is alkaline; in the carnivora it is acid.

The Inorganic Salts are made up of sodium, potassium, calcium and magnesium, chlorides and phosphates, and a small amount of iron.

The Chief Proteid of milk is caseinogen; lacto-albumin and lacto-globulin are found associated with it in small amount. Caseinogen may be precipitated by saturating milk with acetic acid, magnesium sulphate or sodium chloride.

Caseinogen may be obtained as follows: Saturate milk with sodium chloride, thus precipitating caseinogen and fat; filter, wash the precipitate with saturated solution of sodium chloride, rub moist precipitate with water and allow to stand twenty-four hours, and filter. Caseinogen is contained in the filtrate. A portion of the solution treated with acetic acid gives a precipitate of caseinogen; another portion treated with rennin, calcium chloride and heat (40° C.) precipitates para-casein.

To separate lacto-globulin and lacto-albumin, proceed as follows: Saturate a portion of the milk with sodium chloride and filter, to the filtrate add magnesium sulphate to saturation; lacto-globulin precipitates. Filter and add to the filtrate ammonium sulphate to saturation; lacto-albumin precipitates.

The action of rennet upon milk results in the cleavage of caseinogen into casein, an insoluble proteid, and a small quantity of a soluble proteid. This cleavage is indicated by the formation of a coagulum, consisting of casein, and the insoluble proteid, with fat globules entangled in the coagulated mass. The coagulation does not occur in the absence of calcium salts.

The liquid portion of coagulated milk is called whey, and it contains water, salts, lacto-albumin and milk-sugar. The solid portion is called curd, and consists of casein and fat.

Milk-sugar belongs to the saccharose group and has the formula, $C_{12}H_{22}O_{11}.H_2O$. By action of the lactic acid ferment

it is readily converted into lactic acid and carbon dioxide. The formation of lactic acid in milk gives a sour taste and causes the precipitation of caseinogen. Milk-sugar is dextro-rotatory; it yields galactose and dextrose by hydrolysis.

Milk-fat may be removed by shaking with ether after the addition of a few drops of solution of caustic alkali to dissolve the proteid envelope of the fat-globules.

Milk-fat is a mixture of the glycerides of palmitic and oleic acids, chiefly, with smaller quantities of butyric, stearic, caproic and caprillic acids.

The fat-globules of milk do not cohere spontaneously, but they may be made to do so after the formation of lactic acid in milk, by churning. Butter represents the milk fat, containing a small percentage of water, traces of casein, salts and coloring matter.

Human Milk differs from cow's milk, as may be seen in the preceding analysis, in that cow's milk contains over twice as much proteid and inorganic salts, and nearly a third less of milk-sugar. The casein of human milk is more readily soluble in gastric juice, and the precipitate of para-casein is more finely divided than in cow's milk. The casein of human milk contains less of carbon, nitrogen and phosphorus, but more of hydrogen, sulphur and oxygen, than cow's milk. Human milk is said to contain a proteid called *opalisin,* which is rich in sulphur, and which is not found in other milk.

THE URINE.

The urine is an excretion derived from the blood by the Malpighian corpuscles and uriniferous tubules of the kidney. It is an aqueous solution of organic and inorganic constituents, which are formed during tissue metabolism, and represent the waste products of cellular activity.

Normal human urine, when fresh, is a clear, transparent

liquid; it has a pale yellow or amber color and an aromatic odor; its reaction is acid; its specific gravity is 1.020.

The urine upon standing will form a thin, cloudy film of mucus, which gradually sinks to the bottom of the vessel; the acid reaction increases, and, if the urine be concentrated, a deposit of urates or uric acid gradually forms. After a time, if the temperature be slightly elevated, the urine gradually undergoes decomposition by the presence of micro-organisms. This change is largely due to the *micrococcus ureæ* and the *bacterium ureæ*. If left at rest, the urine frequently forms a thin, lustrous film on the surface, which is composed of bacteria and vegetable growth. An ammoniacal odor develops from the formation of ammonium carbonate from decomposing urea. The reaction becomes alkaline and a turbidity results from precipitation of earthy phosphates, ammonio-magnesium phosphate and ammonium urate.

The conversion of urea into ammonium carbonate is accomplished by the action of bacteria. The bacteria cause a molecule of urea to combine with two molecules of water, as shown in the following equation:

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3.$$

The composition of urine is shown in the following analysis according to Brubaker:

Water	1,500.00 cc.
Total solids	72.00 gm.
Urea	33.18 gm.
Uric acid (urates)	0.55 gm.
Hippuric acid (hippurates)	0.40 gm.
Kreatinin, xanthin, hypoxanthin, guanin, ammonium salts, pigment, etc.	11.21 gm.
Inorganic salts: Sodium and potassium sulphates, phosphates and chlorides; Mg and Ca phosphates	27.00 gm.
Sugar	a trace.
Gases: Nitrogen and carbonic acid.	

The composition of urine, given in the above analysis, varies greatly with varying conditions. It is influenced by the degree of activity of the subject, the time of day, temperature, age, sex, &c.

Physical Properties.

The daily quantity of urine passed varies with varying conditions of food, drink, temperature, health and disease. It averages, in the normal healthy adult, from 1,000 to 1,500 c.c. (36 to 54 fluid ounces). The daily quantity of total solids varies from 55 to 60 grams (840 to 920 grains).

The Color of urine varies from pale yellow or colorless to reddish-brown, but it is usually of an amber color. A smoky, reddish urine indicates the presence of blood; a brownish-green indicates presence of bile; colorless urine in large quantity indicates presence of sugar.

The color of urine is affected by certain articles of diet and certain drugs. It is darkened by large quantities of meat and coffee; beets produce a reddening effect; carrots produce a brown color; rhubarb and senna, a reddish-yellow. Large doses of salicylic acid color the urine green; carbolic acid produces a dark or black coloration.

The Urinary Pigments are: Urobilin, urochrome, and uroerythrin. They are believed to be produced from bilirubin of the liver. The presence of indican, from intestinal fermentation, also gives rise to color when the urine is exposed to the air or acted upon by reagents.

Urochrome imparts a yellow or orange color. It may be precipitated by ammonium sulphate, and the precipitate when decomposed by an acid gives a dark, brown substance.

Urobilin imparts a reddish-brown color. It is increased by conditions which cause destruction of hemoglobin in the body, in high fever and in cirrhosis of the liver.

Uroerythrin imparts the pink or red color to urine. It is said to be increased by excessive eating, alcoholic excesses, malaria, pneumonia, excessive perspiration and great muscular exertion. Its presence in excessive quantity is indicated by the appearance of a pink color in the precipitate caused by adding a solution of barium chloride to the urine.

Odor. Fresh urine has a pleasant, aromatic odor, believed to be due to the presence of volatile acids and ethers. The disagreeable ammoniacal odor is due to the products of decomposition, and if this is present at the time the urine is passed it indicates that decomposition has taken place inside the body. The decomposition of urine containing albumen or pus may give rise to the formation of hydrogen sulphide.

Odors are imparted to the urine by ingestion of certain articles of food, such as asparagus, cabbage, cauliflower, parsnips and onions or garlic.

Reaction. In normal, fresh urine the reaction is usually acid. The acidity is due to the presence of mono-sodium hydrogen phosphate, NaH_2PO_4. The reaction finally becomes alkaline upon standing, when ammoniacal decomposition has taken place.

The acidity of urine is diminished or disappears after a full meal, especially of a vegetable diet; it is increased by excessive meat diet, and by prolonged muscular exercise.

Alkaline acetates, tartrates and citrates increase the alkalinity of the urine; benzoic and boric acids increase the acidity.

Alkalinity due to the presence of ammonia may be recognized by the return of the red color of litmus upon drying, after it has been dipped into the urine.

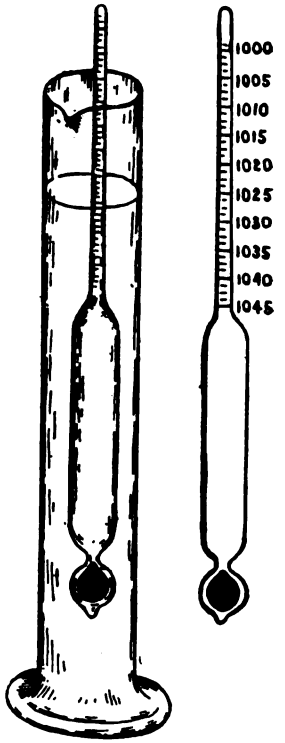
Specific Gravity. The specific gravity of normal urine averages about 1.020 (1.021[1]), though it may vary in health from 1.012 to 1.030. In determining the specific gravity it must be

[1] Ogden.

remembered that the daily quantity of the urine must be taken into consideration in order to properly estimate its value. A urine may have a high specific gravity on account of a limited consumption of fluids and excessive perspiration, or a low specific gravity may be occasioned by the opposite conditions.

A long continued variation from the normal should excite the suspicion of disease. In diabetes insipidus the specific gravity may range as low as 1.001 or 1.002, while in diabetes mellitus it is usually high, sometimes reaching 1.050. On the other hand, the specific gravity of diabetic urine may be normal or below on account of the excessive amount of fluid excreted by the kidney.

FIG. 48.



Urinometer.

The determination of specific gravity is made by the use of a specially constructed hydrometer, known as a *urinometer,* the scale of which is graduated from 1.000 to 1.060. This instrument is made to float in the urine in a narrow glass vessel, when the specific gravity may be read from the scale; care should be taken to prevent the urinometer from coming in contact with the sides of the containing vessel. The temperature at which the determination is to be made is usually marked on the instrument, and should, of course, be duly regarded.

Total Solids. In the healthy adult male the daily quantity

of total solids amounts to about 70 to 73 grams, of which, nearly one-half is urea, one-fifth chlorides, and one-twenty-fifth phosphates.

The total solids per 1,000 c.c. of urine may be estimated approximately by multiplying the last two figures of the specific gravity by the coefficient of Haeser, which is 2.33, the product being expressed in grams. For example, suppose the specific gravity of the urine to be 1.020; the solids per 1,000 c.c. would be

$$20 \times 2.33 = 46.60 \text{ grams.}$$

If the daily quantity of urine were 1,500 c.c., then the total solids in this amount of urine would be

$$\frac{46.60}{1000} \times 1500 = 69.9 \text{ grams.}$$

The total solids of urine may be more accurately determined by taking 10 c.c. of the mixed 24 hours urine, placing it in a weighed platinum capsule and evaporating carefully to dryness in a vacuum over sulphuric acid. The dry residue is weighed, and when the weight of the dish is deducted, the remainder represents the weight of the total solids in 10 c.c. of urine. From this the solids in the whole volume of the urine may be calculated.

By incinerating the dried residue and weighing the ash, the total inorganic solids may be determined. The difference between the weight of the total solids and total inorganic solids, represents the weight of total organic solids.

Analysis of the ash may be practiced for determination of inorganic constituents. Chlorine is determined by precipitating a solution of the ash in dilute nitric acid by adding silver nitrate; sulphuric acid by barium chloride; phosphoric acid by ammonium molybdate; calcium by ammonium oxalate; potassium by platinum perchloride; iron by potassium ferrocyanide,

&c. Most of the inorganic constituents may be determined more conveniently, however, by tests applied directly to the urine.

Normal Constituents.

1. INORGANIC.

Chlorides occur in the urine chiefly as sodium chloride, though small quantities of potassium and ammonium chloride are found. Chlorides constitute the chief solid constituent of urine next to urea. The daily quantity of sodium chloride eliminated in the urine varies from 10 to 20 grams.

The chlorides in the urine are increased by increased consumption of sodium chloride; they are diminished, or absent, in pneumonia; diminished in the early stages of most acute diseases, and in chronic diseases attended by serous effusions.

Detection and approximate estimation of the chlorides may be accomplished by taking half a wineglass of urine, with one-third its volume of nitric acid in a separate layer at the bottom, and adding a drop of solution of silver nitrate (1 part to 8 of distilled water). The presence of chlorides will be indicated by the formation of a white precipitate of silver chloride. If the chlorides be normal or increased, the precipitate forms a white ball, which falls to the bottom of the urine; if the chlorides be diminished, the precipitate becomes quickly diffused through the surrounding liquid. Albumen interferes with this test and, if present, it should be removed by boiling, adding a drop of acetic acid, and filtering.

Estimation of Chlorine by Mohr's Volumetric Method. The solutions necessary for this test are: 1. A 20 per cent. solution of pure neutral potassium chromate in distilled water. 2. Standard silver nitrate solution, made by dissolving 29.075 grams fused silver nitrate in distilled water and making up to 1,000 c.c. Each c.c. of this solution represents .01 gm. sodium chloride, or .006065 gm. chlorine.

Process. Take 10 c.c. of urine, dilute with 50 c.c. of distilled water, and add .5 c.c. of the potassium chromate solution. The mixture is now to be titrated with the standard silver nitrate solution, until a permanent pink color appears. One c.c. should be deducted from the total quantity of test solution used, so as to allow for the action of other bodies on the test solution.

Phosphates. Phosphoric acid occurs in the urine combined with sodium and potassium, on the one hand, and with magnesium and calcium on the other. The former is known as the *alkaline phosphates* and comprises about two thirds of the phosphates present; the latter is known as the *earthy phosphates,* and comprises about one third of the total.

The composition of these phosphates in normal acid urine is represented in the following formulæ:

NaH_2PO_4, Na_2HPO_4, $CaHPO_4$, $CaH_4(PO_4)_2$ and $MgHPO_4$.

The earthy phosphates frequently precipitate in an alkaline urine, on account of the conversion of acid phosphate of calcium and magnesium into normal salts. The grayish sediment so formed is often referred to as *amorphous phosphates.* A similar change is sometimes produced by boiling a feebly acid urine, which gives rise to a grayish-white precipitate. This precipitate may be mistaken for albumen, but it can be easily distinguished from the latter by its solubility in a few drops of acetic acid. Ammoniacal urine sometimes forms the, so-called, " triple phosphate," by the combination of ammonium with magnesium phosphate, $MgNH_4PO_4$. This substance is sometimes formed in the bladder as a result of ammoniacal decomposition of the urine, giving rise to the formation of urinary calculi, or " stone in the bladder."

Earthy phosphates are precipitated by adding a solution of caustic alkali to the urine.

The alkaline phosphates, being very soluble, are not so easily precipitated from the urine.

The normal quantity of phosphoric oxide (P_2O_5) excreted in the 24 hours urine is from 2.5 to 3.5 grams.

The phosphates are increased in diseases of the bones, rickets, tuberculosis, diseases of the nervous system and acute yellow atrophy of the liver; they are diminished in most of the acute diseases, diseases of the kidney, gout and pregnancy.

Detection and Approximate Estimation of Phosphates.

Earthy Phosphates. To half a test-tube of filtered urine add enough ammonia water to produce a decided alkaline reaction, and warm the mixture. The earthy phosphates are precipitated as a grayish-white powder. Allow the tube to stand for 18 hours and if the sediment is one-fourth to one-half inch deep the quantity is normal; if more than one-half inch, increased; if less than one-fourth inch, decreased.

Alkaline Phosphates. After separating the earthy phosphates, as described above, filter the liquid, add 5 cc. of magnesia mixture[1] and warm; the alkaline phosphates form a white precipitate. Allow to stand for 18 hours, and if the deposit be one-half to three-quarters inch deep the quantity is normal; if more than three-quarters inch, increased; if less than one-half inch, diminished.

The total phosphoric acid may be estimated by taking 50 c.c. of the urine, adding a few drops of solution of calcium chloride and then ammonia water. The precipitate is washed on the filter, dried, ignited and weighed. The weight of the precipitate represents tricalcium phosphate, Ca_32PO_4, from which the phosphoric acid may be calculated.

Sulphates. Sulphates are present in the urine in two forms, viz.: Sodium, potassium and magnesium sulphates; sulphates

[1] *Magnesia Mixture.*—Made by dissolving one part each of magnesium sulphate, ammonium chloride and ammonia water in 8 parts of distilled water.

of indoxyl, skatoxyl and phenol. The former are known as alkaline sulphates; the latter, as aromatic sulphates.

The normal daily quantity of sulphates excreted is 1.5 to 3.0 grams, one-tenth of which is in the form of aromatic sulphates. The quantity may vary considerably in health: it is increased in acute febrile diseases; it is diminished in chronic diseases.

Detection and Approximate Estimation of Sulphates may be made according to the method of Ogden, as follows: To half a test-tube of the filtered urine add from one to two finger-breadths of barium solution,[1] a white precipitate forms, which in 18 to 24 hours will fill one-half the concavity of the tube in normal urine; if diminished, less than one-half the concavity; if increased, more than one-half the concavity.

Sulphuric acid is estimated by the method of Salkowski, viz.: 100 c.c. of the urine in a beaker is acidified with 5 c.c. of strong hydrochloric acid, the mixture is boiled and barium chloride solution is added as long as a precipitate is formed. The precipitate is collected on a filter, washed with hot water, until the washings give no precipitate with sulphuric acid; then wash with hot alcohol and then with ether. Remove the filter and contents, and incinerate in a platinum crucible. Cool over sulphuric acid, weigh, deduct weight of dish and filter-ash. The remaining weight represents barium sulphate, $BaSO_4$, from which SO_3 may be calculated—100 parts barium sulphate is equivalent to 34.33 of SO_3.

Correction. A small amount of barium sulphide is formed in the analysis, which is corrected by adding a few drops of sulphuric acid after the platinum dish has cooled, and heating again to redness, to drive off excess of sulphuric acid.

2. Organic.

Urea, Carbamide, $CO(NH_2)_2$. Urea is by far the most important of the organic constituents of urine. It represents

[1] Barium solution is made by dissolving barium chloride, 4 parts; strong hydrochloric acid, 1 part; in 16 parts of distilled water.

the end product of proteid metabolism, and is obtained solely from animal sources. It occurs in small amount in various tissues of the body, viz.: Muscle, blood, chyle, lymph, bile and other fluids. It contains 85 to 90 per cent. of the total nitrogen of urine.

Urea may be prepared by evaporating a convenient quantity of urine to a syrupy consistency and adding an equal volume of nitric acid to the cooled liquid. The urea separates in the form of crystals of the nitrate of urea, which may be decomposed into urea and barium nitrate, by adding barium carbonate.

In properties, urea is a solid, forming colorless, prismatic crystals which have a cooling, bitter taste, resembling potassium nitrate. It dissolves in water and fuses when moderately heated (130° C.), but it decomposes at a high temperature, forming ammonia gas and water vapor.

Urea undergoes decomposition when boiled with water, and the decomposition is facilitated by pressure, forming ammonia, carbon dioxide and water, thus:

$$CO(NH_2)_2 + 2H_2O = CO_2 + 2NH_3 + H_2O.$$

Hypobromites and hypochlorites of the alkalies cause its decomposition, forming hydrochloric acid, carbon dioxide and nitrogen. Upon this reaction the most important method for its quantitative estimation is based. The decomposition is effected by the bromine or chlorine of these compounds, thus:

$$CO(NH_2)_2 + 6Br = H_2O + 6HBr + CO_2 + N_2.$$

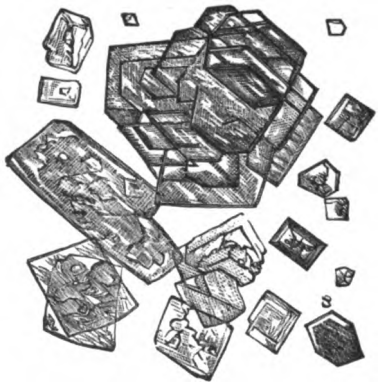
Urea forms salts with acids, retaining the hydrogen like alkaloids.

The quantity of urea under normal conditions in the 24 hours urine varies from 17 to 40 grams (usually from 30 to 40 gm.).

Urea is diminished in health when the diet is comparatively free from nitrogenous food, following excessive perspiration, sometimes in pregnancy, after taking small doses of quinine,

following the ingestion of excessive quantities of water for a long time. It is diminished in disease, in most of the kidney diseases, in degenerative changes of the liver, in acute febrile diseases following the acme of the disease and in convalescence, in diseases attended with serous effusion, preceding death from any cause, excessive vomiting and diarrhea.

FIG. 49.



Urea Nitrate. (Coblentz.)

Urea is increased in health by over-feeding, by great muscular exertion, by ingestion of ammonium compounds, by hot baths. It is increased in disease in the early stages of febrile diseases, in diabetes insipidus, in diabetes mellitus, sometimes in chronic interstitial nephritis, in chronic gout.

Urea May be Detected in Urine. 1. By adding to the urine an equal volume of solution of sodium hypobromite; effervescence takes place in the presence of urea from the escape of nitrogen gas.

2. To a drop of urine on a glass slide add a drop of pure nitric acid and allow the liquid to evaporate. Crystals of urea nitrate may be seen under the microscope.

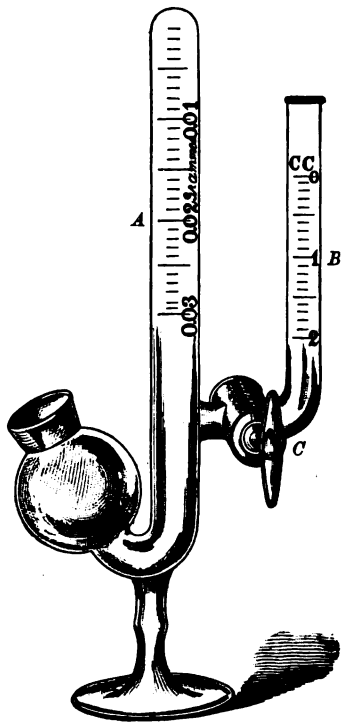
Estimation of Urea. Several methods have been devised for the quantitative estimation of urea, the simplest and most convenient of which is the hypobromite method of Knop. This is based upon the decomposition of urea, in urine, by alkaline sodium hypobromite solution, and the measurement of the volume of nitrogen evolved. In this decomposition, nitrogen, carbon dioxide and water are formed, as shown in the equation:

$$CO(NH_2)_2 + 3NaBrO = 3NaBr + CO_2 + N_2.$$

An excess of caustic soda is used in the reaction to absorb the carbon dioxide, the nitrogen, being left free, is collected and measured. Since one gram of urea furnishes 370 c.c. of nitrogen at 0° C., 760 mm. pressure, the quantity of urea may be calculated from the volume of the nitrogen evolved.

The solutions for making this test should be freshly made, as follows: A solution of caustic soda is kept for use containing 100 grams sodium hydroxide dissolved in 250 c.c. of water. Bromine is kept in a separate bottle. When it is desired to make the test, 10 c.c. of caustic soda solution are mixed with 1 c.c. of bromine, and the mixture is then diluted with an equal volume of water.

FIG. 50.



Hinds-Doremus Ureometer. (Holland.)

The test is made with the aid of the Doremus Ureometer, as shown in the cut. The above mixture is introduced into the main tube of this instrument and 1 c.c. of urine is allowed to flow into the liquid from the side tube in small portions at a time by turning a stopcock. As nitrogen gas is disengaged, it rises in the tube of the instrument, displacing the liquid and the volume may be read off from a graduated scale.

The instrument is usually graduated to represent fractions of a gm. of urea to the cubic centimeter of urine, ranging from 0.01 to 0.03 gm. The percentage of urea may be expressed from this reading by removing the decimal point two figures to the right, thus: 0.01 gm. is 1 per cent. of urea.

Uric Acid, $H_2C_5H_2N_4O_3$. Uric acid occurs in the urine in combination chiefly, as the urates of sodium, potassium, ammonium, and to a less extent in combination with calcium and magnesium. Its exact source and manner of formation are not known at the present time, but it is believed to be derived from

FIG. 51.

Uric Acid Crystals. *a*, rhombic forms; *b*, barrel form; *c*, sheaves; *d*, rosettes. (Bartley's Clinical Chemistry.)

the nucleins of nucleo-proteids, and to be formed in the spleen.

Uric acid, *when pure,* is a white, crystalline solid. It crystallizes from the urine in yellowish-red crystals, of prismatic shape. It is odorless and tasteless; soluble in 16,000 parts of cold water, or 1,600 parts of boiling water; insoluble in alcohol or ether. On account of its great insolubility it frequently

separates from solution in the body, forming deposits in the tissues and urinary tract.

Uric acid may be prepared as follows: Add 100 c.c. hydrochloric acid to 1,000 c.c. of urine, allow to stand for 24 hours, collect the crystals on a filter, wash with water, transfer to a beaker and dissolve in caustic soda solution. The solution is decolorized with bone black, hydrochloric acid is added to reprecipitate the urea, and the purified crystals, so obtained, are collected, washed and dried.

The normal daily quantity of uric acid varies from 0.2 to 1.2 gram.

Uric acid is increased in excessive nucleo-proteid diet and insufficient exercise; in many acute diseases, especially of the lungs; in organic heart disease; in diseases of the liver or spleen; in anemia, gout and diabetes mellitus. It is diminished by a vegetable diet; after continued ingestion of large quantities of water; in most of the chronic diseases, and after large doses of quinine.

Detection of Uric Acid. 1. *Murexide Test.* To a few fragments of uric acid in a porcelain dish add a drop of nitric acid and evaporate. Add a drop of ammonia water to the dry residue, when a purplish-red color will make its appearance.

2. Add magnesia mixture to the urine and then a solution of silver nitrate; uric acid deposits as a gelatinous precipitate.

3. Uric acid or urate boiled with Fehling's solution gives a yellowish or reddish precipitate, resembling the precipitate formed by glucose.

Estimation of Uric Acid. Heintz's Method. To 200 c.c. of filtered urine add 10 c.c. strong hydrochloric acid and let stand in a cool place for 24 hours. Collect the crystals on a previously dried and weighed filter-paper, wash with cold water, dry at 100° C. and weigh. By deducting the weight of the filter-paper, the quantity of uric acid in 200 c.c. of urine will

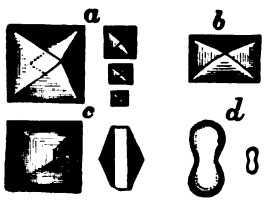
be obtained. This method only gives approximate results, but it is sufficiently accurate for clinical purposes.

Hippuric Acid, $C_9H_9NO_3$, is present in large amount in the urine of herbivorous animals. It is present in small quantities in normal human urine, the daily quantity being 0.5 to 1.0 gram. It is increased by a vegetable diet, in diabetes, in acute febrile diseases and chorea, but it has no special clinical significance.

Hippuric acid may be detected by evaporating a portion of the urine to dryness with a little nitric acid, and heating the dry residue in a test-tube. The odor of bitter almonds is observed if the acid is present.

Oxalic Acid is excreted in small amount in the urine, about 0.1 gm. daily, chiefly as calcium oxalate. When it occurs in excess, indicating deficient oxidation, it frequently forms octahedral or dumb-bell crystals upon standing.

FIG. 52.



Calcium Oxalate Crystals. *a*, octahedra; *b*, basal plane of an octahedron; *c*, compound forms; *d*, dumb-bells. (Bartley's Clinical Chemistry.)

FIG. 53.

Dumb-bell Crystals of Oxalate of Calcium. (Bartley's Clinical Chemistry.)

The elimination of oxalic acid is increased by a diet of tomatoes, beets, spinach, etc., and in diabetes and jaundice.

Indican, *indoxyl-potassium sulphate,* $C_8H_6NOSO_2OK$. This compound is formed from indoxyl, which is produced by intestinal fermentation and putrefaction. It occurs normally in

the urine to the extent of .002 per cent. It is increased by increased fermentation and putrefaction in the intestine.

Tests for Indican. 1. Equal volumes of urine and hydrochloric acid with a few drops of nitric acid are boiled together, cooled and agitated with chloroform. Upon standing, the chloroform separates as a violet-colored liquid, having dissolved the indican.

2. To five c.c. of hydrochloric acid in a flask, add 20 drops of urine with agitation; the color will be light yellow if the proportions of indican be normal; if in excess, the color will be violet or blue. Absence of color indicates absence of indican, though a coloration may appear later on without significance.

Other organic bodies are found in urine, such as creatinin, allantoin, mucin, coloring matters, etc., the determination of which is only a matter of scientific interest.

Abnormal Constituents.

The abnormal constituents of urine are proteids, carbohydrates, bile products, constituents of blood, acetone and diacetic acid.

Albumin. The proteids usually found in the urine are serum-albumin and serum-globulin, but albumoses, peptones, nucleo-albumins and hemoglobin sometimes occur.

Since the tests for albumin are dependent upon its coagulation and precipitation, the urine should be clear when these tests are applied. If the urine be cloudy, filtration will generally serve to remove the turbidity. Sometimes the urine contains a precipitate of the amorphous earthy phosphates; in order to remove these, a little magnesium oxide may be rubbed with the urine and the liquid subjected to filtration. Turbidity due to the presence of urates will disappear upon warming.

Tests for Albumin. 1. *Heat Test.* Add one or two drops of 10 per cent. acetic acid to a test-tube half filled with urine.

If the urine be alkaline add sufficient acid to produce an acid reaction. Heat the upper part of the urine to the boiling point and if albumin be present it will be indicated by the appearance of a white precipitate. A precipitate is sometimes caused by the presence of earthy phosphates, but these quickly dissolve upon the addition of a few drops of acetic acid, which causes an increased precipitation of albumin.

If one-fourth volume of a saturated solution of sodium chloride be added to the urine before applying this test, the precipitation of globulin is aided, and mucin is kept in solution.

A precipitate caused by the addition of acetic acid is due to the presence of mucin or nucleo-albumin, and should be removed by filtration.

2. *Nitric Acid Test.* About half an inch of pure nitric acid is placed in a test-tube and the urine is poured down the side of the tube so as to form a separate layer upon the acid. If albumin be present a white band, or zone, makes its appearance at the line of contact of the two liquids.

The presence of urates in a concentrated urine sometimes gives rise to the formation of a white zone resembling albumin. The white zone from urates is not sharply defined like that from albumin, but it is diffused into the surrounding urine; the precipitate of urates will disappear upon warming, but albumin remains permanent.

3. *Ferrocyanide Test.* A mixture consisting of 1 part of 50 per cent. acetic acid, and 2 parts 10 per cent. ferrocyanide solution is placed in a test-tube, and urine is carefully poured down the side of the test-tube so as to form a separate layer. If albumin be present, a white zone makes its appearance at the line of contact of the two liquids. This zone may be caused by the presence of urate, but in such a case it disappears upon heating.

4. *Roberts' Contact test* is made like the above, using a solu-

tion of 1 part strong nitric acid and 5 parts saturated solution magnesium sulphate. Albumin is indicated by the appearance of a white band at the line of contact of the two liquids. Alkaloids, resins and albumoses give the white zone, it disappears upon warming when caused by these bodies, and may thus be distinguished from albumin.

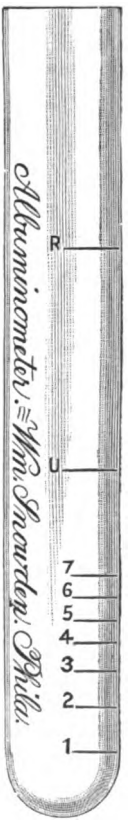
This test is said to be sufficiently delicate to detect 1 part in 50,000 or less.

Estimation of Albumin. For the approximate estimation of albumin Esbach's albuminometer is used. This is a graduated test-tube, which is filled with urine to the mark "U," and with reagent to "R"; the mixture is shaken and allowed to stand for 24 hours when the amount of albumin, in grams per liter, is read off on the graduated scale. The standard solution consists of 10 gm. picric acid, 20 gm. citric acid, dissolved in distilled water to make a liter.

The Gravimetric Method consists of acidifying 100 c.c. of urine with acetic acid and precipitating the albumin by heat. The precipitate is filtered out, dried and weighed.

Blood. Presence of blood in the urine generally imparts a red, or brownish color, or a smoky appearance. The presence of 1 part in 1,500 is said to give a smoky urine, and 1 part in 500, a bright red or chocolate-brown, depending upon the degree of decomposition of the blood. The entire blood or simply hemoglobin may be present.

FIG. 54.



Esbach's Albumenometer. (Holland.)

Blood in the urine may be recognized by use of the microscope by the appearance of normal or altered corpuscles; it may

also be recognized by chemical tests, which are of special value when the blood has undergone disintegration.

Tests. 1. Add a few drops of ozonized ether to a few c.c. of tincture of guaiac in a test-tube and then add the suspected urine, so as to form a separate layer at the bottom of the test-tube. If hemoglobin be present, a blue ring will make its appearance at the line of contact of the two liquids, which does not disappear on heating.

2. Make the urine alkaline with caustic soda and boil; the precipitate of phosphates is colored red if coloring matter of blood be present. Collect the precipitate on a filter, wash and dissolve in acetic acid; the solution becomes red if blood pigment be present, and by exposure to air the color gradually disappears.

Pus. Pus in the urine gives a cloudy appearance, and forms a grayish-white deposit upon standing. Pus may be recognized by examining the sediment under the microscope, when pus corpuscles will be seen having the same appearance as leucocytes. A drop of 20 per cent. acetic acid passed under the slide will cause the granules of the corpuscles to dissolve, the nucleus to become more distinct and the cell to swell.

A chemical test for pus is to add to the urinary deposit, after decantation of the urine, a few cubic centimeters of caustic potash solution. If pus be present, a thick, tenacious, viscid mass is formed, which adheres to the sides of the vessel and can be drawn out into strings when a glass rod is dipped into the mass.

Sugar. *Glucose,* $C_6H_{12}O_6$, is the form of sugar usually found in urine. It is said to be present in normal urine to the extent of .01 per cent. It is present in large quantities in diabetes mellitus, sometimes as much as 10 per cent., but more frequently the percentage in this disease varies from 3 to 5. The presence of sugar is sometimes indicated by a high specific

gravity, 1.030 to 1.050, but increased secretion of fluids may give a low specific gravity to a urine containing sugar the daily quantity of which may be very considerable.

As has been explained in the preceding pages, many of the tests for glucose depend upon its reducing action upon certain metallic oxides in the presence of alkalies. In applying these tests, a precipitate of earthy phosphates is sometimes produced, which might be mistaken for sugar. For this reason, it is well to remove these phosphates before testing for sugar, by adding a few drops of potassium hydroxide solution and filtering out the precipitated earthy phosphates.

Before applying the tests for sugar, albumin should be tested for, and should be removed from the urine, if present.

Tests. 1. *Haines' Test.* Make a solution by dissolving 30 grains of pure cupric sulphate in one-half an ounce of distilled water; add one-half ounce of pure glycerine, mix, and add 5 ounces of liquor potassa.

The test is applied by gently boiling about 1 dram of the solution in a test-tube and adding 6 or 8 drops of the suspected urine. A copious yellow, or yellowish-red, precipitate forms if sugar be present.

2. *Fehling's Test.* Make two solutions, according to the following formulæ:

Crystallized cupric sulphate	34.64 gm.
Water to make	500.00 c.c.
Pure crystallized potassium sodium tartrate	173.00 gm.
Potassium hydroxide	125.00 gm.
Water to make	500.00 c.c.

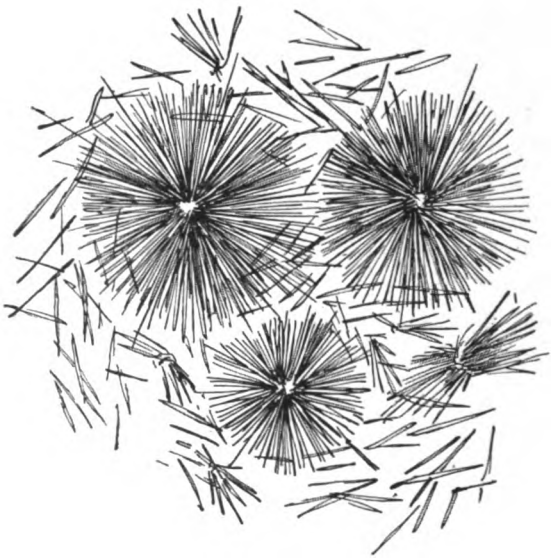
These solutions are to be kept in separate bottles and equal volumes of the two are to be mixed at the time they are to be used. The mixed solution serves as a qualitative and also as a quantitative test.

When the solution is boiled, and urine added in small por-

tions at a time, after removal from the flame, sugar is indicated by a yellow, or yellowish-red, precipitate.

3. *Boettger's Test.* Add an equal volume of liquid potassa, and a little subnitrate of bismuth, to the urine and boil. If sugar be present, a gray or black color is produced. Presence

FIG. 55.



Crystals of Phenyl-glucosazone.

of sulphur gives the same reaction, and consequently, the test is of no value in albuminous urine.

4. *Fermentation Test.* See glucose.

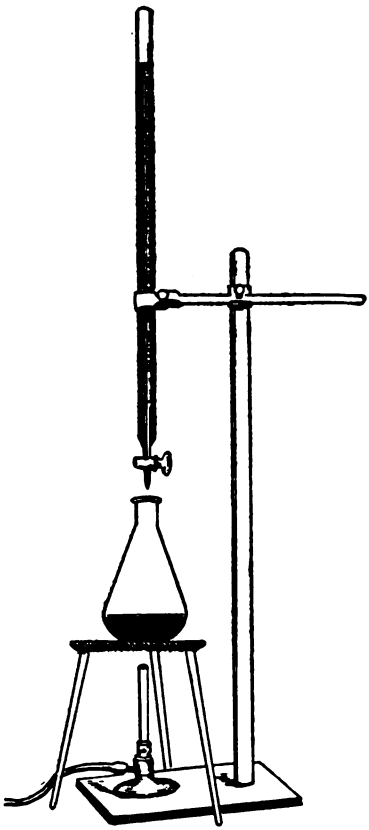
5. *Phenyl Hydrazine Test.* Boil 8 c.c. of the urine with 1 gm. sodium acetate and .5 gm. phenyl-hydrazine. A yellow or orange color makes its appearance in presence of sugar. Allow to cool and add acetic acid; a yellow precipitate of phenyl-glucosazone makes its appearance in needle-shaped crystals.

6. *Quantitative Estimation.* Place 10 c.c. of Fehling's solution in a 200-c.c. flask, add 40 c.c. distilled water and place on

wire gauze over the Bunsen burner. Take the specific gravity of the urine and, if over 1.030, dilute to 1 in 10 of distilled water (1 part urine and 9 parts distilled water); if the specific gravity is less than 1.030, dilute to 1 in 5 (1 part urine and 4 parts water). Place the diluted urine in a buret over the flask. Bring the Fehling's solution to a boil and add the urine, drop by drop, until the blue color of the former has disappeared from the meniscus.

Since 10 c.c. of Fehling's solution will be decomposed by .05 gm. of glucose, the quantity of sugar present may be easily calculated from the number of cubic centimeters of urine used in the titration.

FIG. 56.



Titration in Fehling's Test.

Bile. The color of urine containing bile is usually yellow, greenish-yellow or brown. When such urine is shaken, the froth is quite permanent, and is yellow in color. Filter-paper or linen is permanently stained by the urine.

The reactions for bile depend upon the presence of biliary acids and biliary coloring matters.

Gmelin's Test for Bile Pigments. Place a small quantity of

old, yellow nitric acid in the bottom of a test-tube and float some of the suspected urine on its surface. The presence of bile pigment is shown by a play of colors at the line of contact, beginning with green and passing to blue, violet, red and yellow.

Another way to apply the same test is to mix a strong solution of sodium nitrate with the urine and pour this upon the surface of strong sulphuric acid in a test-tube. In the presence of bile pigments, the colors make their appearance, as above.

Still another modification is to place a few drops of urine on a porcelain plate, and bring a few drops of nitric acid, to which have been added a drop of sulphuric acid, near to the urine, so that the two liquids will gradually coalesce. The same play of colors appears if bile be present.

Pettenkofer's Test for Bile Acids consists in dissolving a few grains of cane sugar in a small quantity of urine in a test-tube, allowing strong sulphuric acid to flow down the side of the test-tube so as to form a separate layer at the bottom. Presence of bile acids is indicated by appearance of a purple band at upper surface of the acid. Upon shaking this mixture the liquid becomes turbid, then clear, and it turns yellow, red and finally purple-violet.

Diazo-reaction is obtained in the urine of patients with typhoid fever, measles, sepsis and tuberculosis. Two solutions are necessary and should be kept in the dark: *a*. Dissolve 2 gm. sulphanilic acid in 50 c.c. hydrochloric acid and 1,000 c.c. of water. *b*. Make a .5 per cent. solution of sodium nitrite.

To apply the test, add 1 c.c. of sodium nitrite solution to 50 c.c. of sulphanilic acid solution; to the mixture add an equal volume of urine and shake. Add ammonia water, carefully, so as to form a separate layer on the surface. A positive reaction gives a crimson zone at the line of contact and, when shaken, the liquid is crimson and the froth pink.

Acetone is recognized by acidifying 500 c.c. of the urine with acetic acid and distilling. A few drops of iodine solution (1 part iodine, 2 parts potassium iodide, dissolved in water to make 10 parts) and of potassium hydroxide are added to the distillate. Iodoform is precipitated if acetone is present.

Legal's Test. To one fourth of a test-tube of urine add a few drops of fresh, strong solution of sodium nitroprusside, and a few drops of acetic acid to prevent reaction with creatinin. The mixture is then made alkaline with caustic soda, and, if acetone be present, a red color makes its appearance, which increases to purple-red.

Diacetic acid may be recognized by adding a few drops of ferric chloride to the urine, filtering off the precipitate and adding more of the ferric chloride to the filtered liquid. A deep red color is produced if diacetic acid is present. The color disappears upon boiling.

The same test should be applied to an ethereal extract made by shaking urine, which has been acidified with a few drops of sulphuric acid, with ether. The same reaction is obtained as above if diacetic acid is present. Phenol, antipyrine, salicylic acid or thalline give the same color with ferric chloride, but it does not disappear upon boiling.

Urinary Concretions.

Urinary calculi may be found in almost any part of the genito-urinary tract, but they occur most frequently in the renal tubules, renal pelvis or urinary bladder. In structure they may be either homogeneous or made up of concentric layers deposited around a central nucleus. The nucleus may be a foreign body, a small concretion formed high up in the urinary tract, or a clot of blood or fibrin, around which, under favorable conditions, normal or abnormal constituents of the urine are deposited. These conditions are: Concentration, hyperacid reaction, alkaline reaction, or the presence of an excess of

substances not freely soluble. A combination of two or more of these conditions is usually active in the formation of calculi. Urinary calculi are named from their principal constituent, *e. g.*, uric acid, calcium oxalate, etc. In point of frequency of appearance two thirds to three fourths are chiefly composed of uric acid or urates; next in order, phosphates, oxalates and carbonates. Among substances rarely forming the chief constituent of a calculus are cystin, xanthin, urostealith, fibrin and indigo.

Pure urostealith, xanthin and cystin calculi have been reported; fibrin occurs principally as a nucleus; indigo may be present in such quantities as to impart to the stone its characteristic color.

In making an analysis of a calculus it must be sawed diametrically through. If homogeneous, the sawdust may be used for chemical analysis; if it is composed of concentric layers, a powder must be obtained from each layer by scraping with a knife. The chemical analysis is conducted as follows:

Heat some of the powder on platinum foil and note which of the following phenomena occurs:

A. Complete combustion by charring without ignition.
B. No change, or reduction to incombustible residue.
C. Complete combustion by ignition.

In case "A" the indications are:

Uric acid,
Ammonium urate,
Xanthin.

To differentiate:

Original powder + HNO_3; evaporate + NH_4OH = purple color = Uric acid or ammonium urate.

Original powder + KOH; heat = odor of NH_3 = Ammonium urate.

Original powder + HNO_3; evaporate + KOH = pink color; heat = violet color = Xanthin.

In case "B" the indications are:

Sodium urate,
Calcium oxalate,

Calcium carbonate,
Calcium phosphate,
Ammonium magnesium phosphate.

To differentiate:

Residue soluble in H_2O, alkaline reaction. Original powder + HNO_3, evaporate + NH_4OH = purple color = Sodium urate.

Residue soluble in acetic acid with effervescence. Original powder insoluble in acetic acid = Calcium oxalate.

Residue slightly soluble in H_2O with alkaline reaction. Original powder soluble in acetic acid with effervescence = Calcium carbonate.

Original powder + KOH, heat = odor of NH_3. Original powder soluble in acetic acid without effervescence = Ammonium magnesium phosphate.

Original powder + KOH, heat, does not give odor of NH_3. Original powder soluble in acetic acid without effervescence = Calcium phosphate.

In case "C" the indications are:

Urostealith,
Fibrin,
Cystin.

To differentiate:

Yellow flame, resinous odor = Urostealith.
Yellow flame, odor of burnt hair = Fibrin or blood clot.
Blue flame, pungent odor of SO_2 = Cystin.

Urinary Sediments.

To obtain urinary sediment for examination one of two methods may be adopted: (1) The centrifugal method, by which the urine in conical tubes is revolved 2,000 times per minute, usually requires only 5 minutes for complete sedimentation. (2) The gravity method, by which the urine in a conical sedimentation glass is allowed to stand in a cool place, and requires about 24 hours for complete sedimentation.

Urinary sediments may be divided into two distinct classes: (1) The chemical sediments, which are the products of normal or abnormal chemical processes in various parts of the body; (2) The histological sediments, which are the products of normal and abnormal tissue changes in definite parts of the genito-urinary tract.

The Chemical Sediments.

For the examination of the chemical sediment it is much better to adopt the centrifugal method, as the rapidity with which sedimentation takes place does not allow time for the occurrence of putrefactive changes in the urine with consequent precipitation of secondary crystals or amorphous salts.

To facilitate the differentiation of the chemical urinary sediments, they may be classified according to the reaction of the urine in which they are usually precipitated, those occurring in acid urines, and those occurring in alkaline urines.

1. The most common sediments found in acid urines are uric acid, sodium urate, and calcium oxalate. The rarer sediments are cystin, creatinin, hippuric acid, leucin and tyrosin.

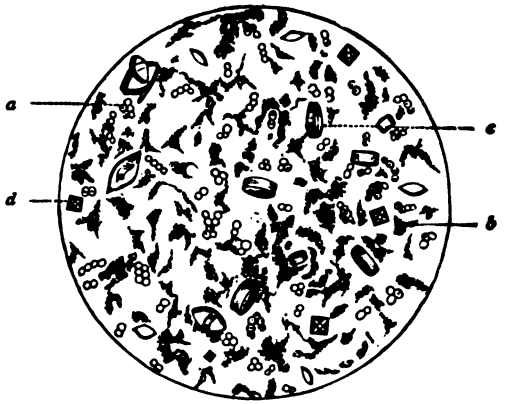
2. The most common sediments found in alkaline urine are ammonio-magnesium phosphate, calcium phosphate, and ammonium urate. Calcium carbonate may occur as a rare sediment in this class. The following is a brief description of the chief differential characteristics, chemical and microscopical, of the members of these two classes:

Uric Acid. Usually large, yellow (rarely colorless) rhomboidal prisms or lozenges with rounded or pointed ends, occurring singly or attached in multiple groups, feebly soluble in hot H_2O, readily soluble in KOH solution, insoluble in HCl, acetic acid or alcohol.

Sodium urate. As a rule, amorphous granules in mass-like aggregations, less frequently colorless, needle-like prisms in stellate or sheaf-like groups readily soluble in hot H_2O, and KOH solution, in HCl and acetic acid with subsequent formation of uric acid crystals.

Calcium oxalate. As a rule, small colorless, highly refractive crystals, consisting of two four-sided pyramids, base to base, usually seen vertically, and resemble the back of a square envelope—lines crossing diagonally from corner to corner,

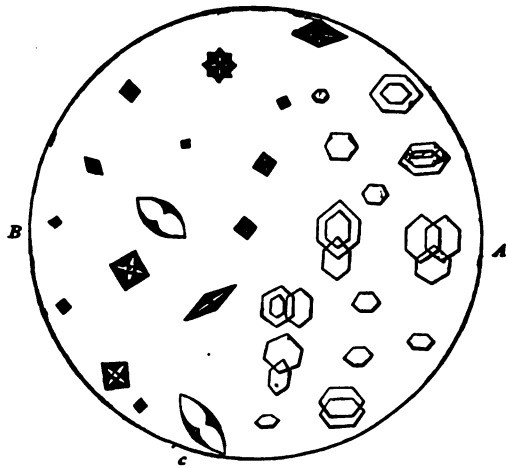
FIG. 57.



a, Fungus; *b*, amorphous sodium urate; *c*, uric acid; *d*, calcium oxalate. (Bartley's Clinical Chemistry.)

crossing in center, less frequently form highly refractive dumb-bell or oval crystals. Insoluble in acetic acid; feebly soluble in KOH solution; soluble in HCl.

FIG. 58.



A, Crystals of cystin; *B*, oxalate of lime; *c*, hour-glass forms. (Bartley's Clinical Chemistry.)

Cystin. Thin, colorless hexagonal plates, usually larger than crystals of calcium oxalate. Insoluble in acetic acid; soluble in HCl; readily soluble in KOH solution.

Creatinin. Colorless prisms or plates, either lozenge or barrel-shaped, sometimes resembling colorless uric acid crystals, but readily soluble in hot H_2O, or alcohol.

Hippuric Acid. Large, colorless plates or prisms, occurring singly or conglomerate, sometimes resembling ammonio-magnesium-phosphate crystals, but are differentiated by being soluble in acetic acid.

FIG. 59.

Hippuric Acid. (Bartley's Clinical Chemistry.)

Leucin. Yellow or brown globules, sometimes showing fine radiating striations.

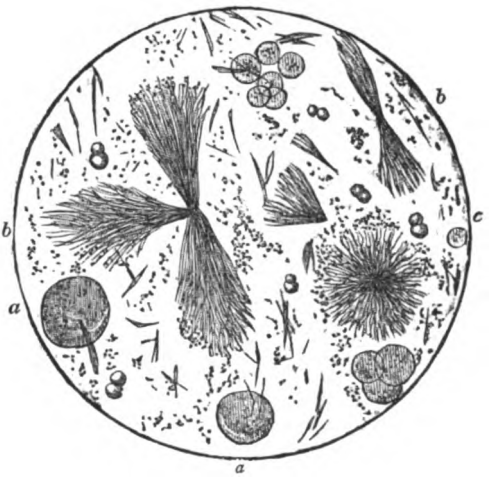
Tyrosin. Exceedingly fine colorless needles, in sheaf-like aggregation.

Leucin and tyrosin usually occur together. Both are readily soluble in hot H_2O, HCl, acetic acid, and KOH solution, and sparingly soluble in alcohol.

Ammonio-Magnesium Phosphate. In distinctly alkaline urine, always colorless, highly refractive, rhomboidal crystal or plates, or three-sided prisms. The rhomboids are bevelled at the sides and ends, the "coffin-lid crystal." In neutral urine, occurs in very irregular plates or partially symmetrical feathery crystals.

Calcium Phosphate. Usually highly refractive amorphous granules either evenly scattered or in clusters but distinctly un-

FIG. 60.



a,a, Leucin balls; *b,b,* tyrosin sheaves; *c,* double balls of ammonium urate. (Bartley's Clinical Chemistry.)

like amorphous sodium urate. Sometimes in slender, colorless rods or very narrow, pointed needle-like pyramids, which are frequently arranged in a radial manner, their points directed to a common center.

All phosphates are readily soluble in acetic acid without effervescence, which easily distinguishes them from crystals for which they might be mistaken.

Ammonium Urate. Brown globules, varying in shape and

size, usually with distinct concentric structure and frequently with radial striation; sometimes with smooth surfaces; perhaps more frequently provided with multiple, curved, thorny projections; soluble in hot H_2O, soluble in KOH solution, soluble in HCl, and acetic acid, with subsequent formation of uric acid crystals.

FIG. 61.

a, Acid ammonium urate; *b*, ammonia-magnesium phosphate; *c*, bacteria. (Bartley's Clinical Chemistry.)

Calcium Carbonate. Small colorless, highly refractive granules of irregular shape; rarely, in combination with magnesium forming small, narrow highly refractive rhomboidal or trapezoidal crystals; soluble in acetic acid with effervescence.

Besides the foregoing chemical sediments, there are some which can not be classified according to the reaction of the urine in which they are usually precipitated; these are, Cholesterin, Hematoidin, and Melanin.

Cholesterin occurs in large, thin, irregular, quadrilateral plates frequently broken at the corners, insoluble in water, dilute acids or alkalies soluble in ether and chloroform; colored violet-red with iodine solution.

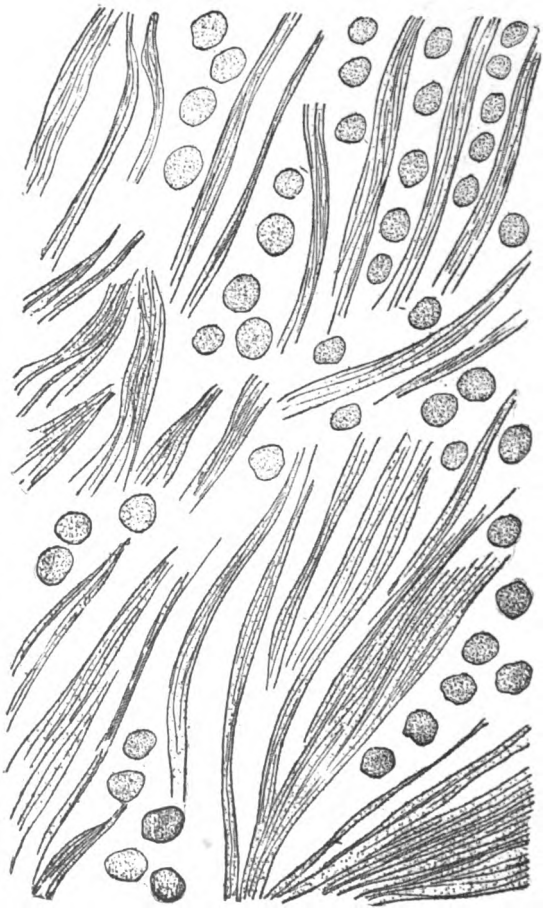
Hematoidin. Occurs either in small needle-like crystals or minute rhombic plates or scales, varying in color from orange-red to brown; soluble in KOH solution, and acquire a green rim on the addition of HNO_3.

Melanin occurs in small black granules, insoluble in water, ether or dilute acid; soluble in NH_4OH, which latter distinguishes it from precipitated carbon.

The Histological Sediments.

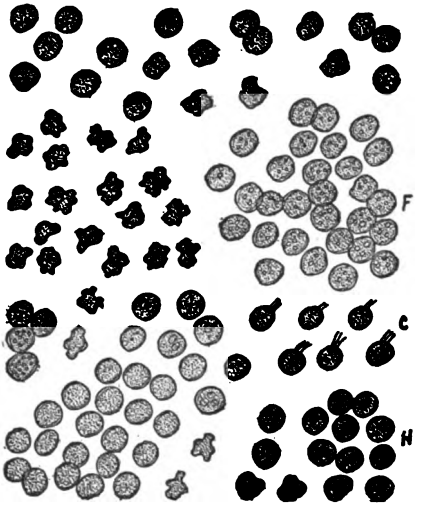
1. These consist of *mucous corpuscles, pus corpuscles, epithelial cells,* and *blood corpuscles,* the appearance of which is shown in the following cuts:

Fig. 62.



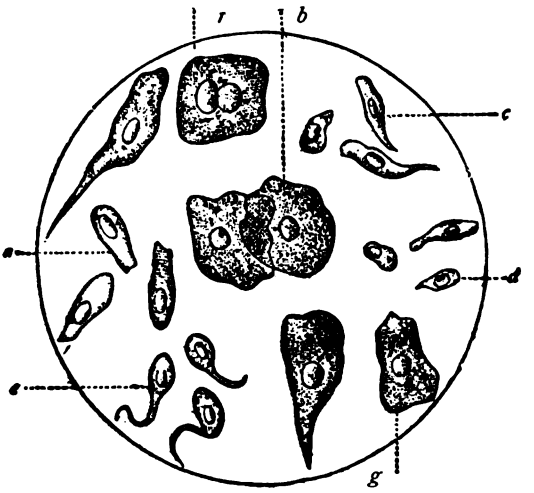
Mucous Threads and Corpuscles (× 500). (After Heitzmann.)

FIG. 63.



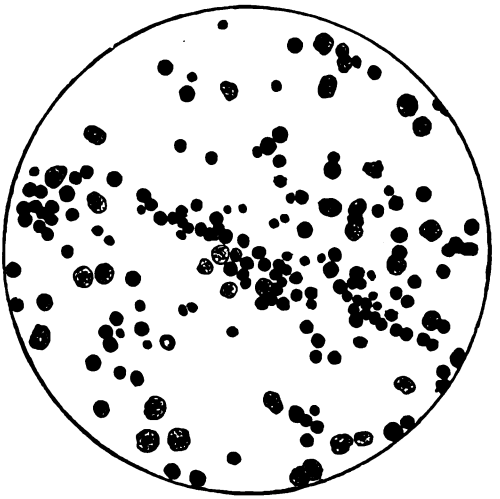
Pus-corpuscles (× 500). *F*, pus-corpuscles with fat-globules; *C*, ciliated pus-corpuscles; *H*, pus-corpuscles with hematoidin crystals. (Heitzmann.)

FIG. 64.



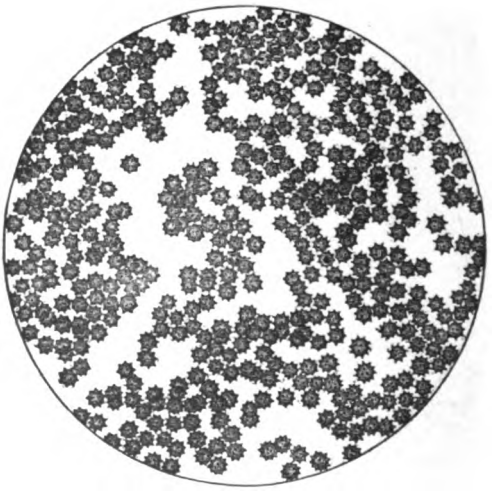
a, Epithelial cells from male urethra; *b*, from vagina; *c*, from prostate; *d*, Cowper's glands; *e*, Littre's glands; *f*, female urethra; *g*, bladder. (Bartley's Clinical Chemistry.)

FIG. 65.



Colored and Colorless Blood-corpuscles. (Holland.)

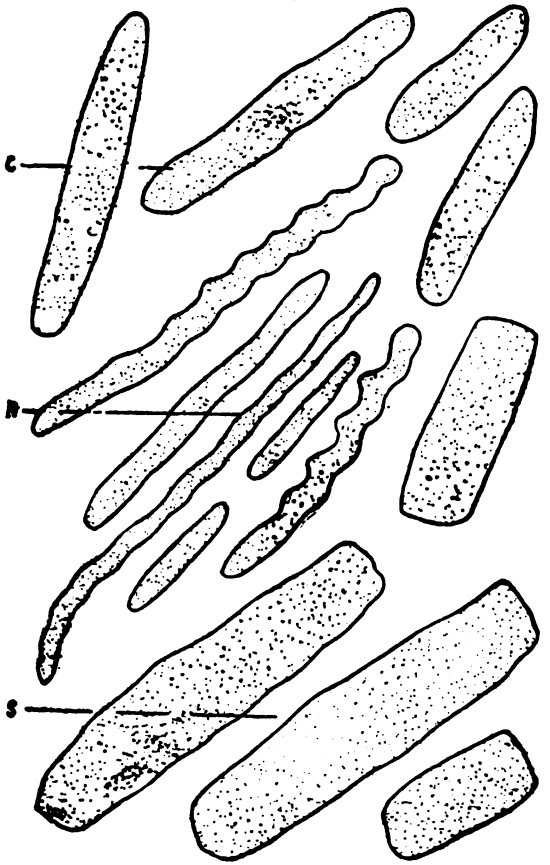
FIG. 66.



Crenated Red Blood-corpuscles in Urine. (Holland.)

2. *Casts* are moulds of the uriniferous tubules, consisting of fibrin. The chief varieties of casts are as follows: *Hyaline casts,* which are clear and transparent; *blood casts,* in which blood corpuscles are imbedded in the fibrinous mould; *epithelial casts,* containing epithelial cells on the surface; *granular*

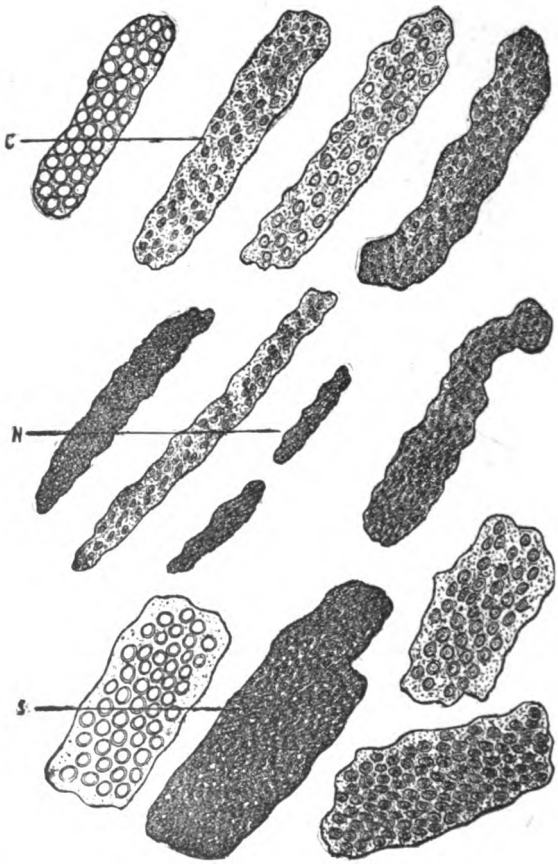
FIG. 67.



Hyaline Casts (× 500). (Heitzmann.) *C,* casts from convoluted tubules; *N,* from narrow tubules; *S,* from straight connecting tubules.

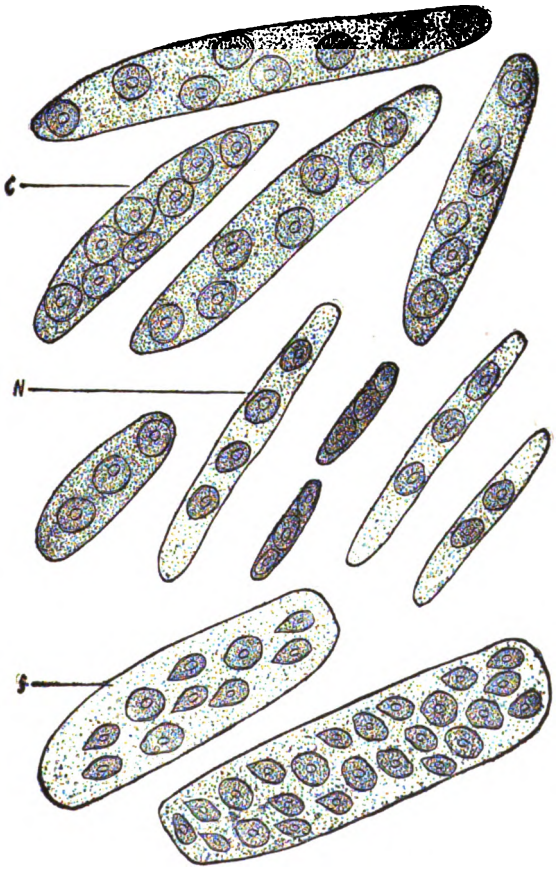
casts, having a granular appearance; *fatty casts,* containing oil drops on the surface; *waxy casts,* more dense than hyaline casts. The appearance of the different casts under the microscope is shown in the following cuts:

FIG. 68.



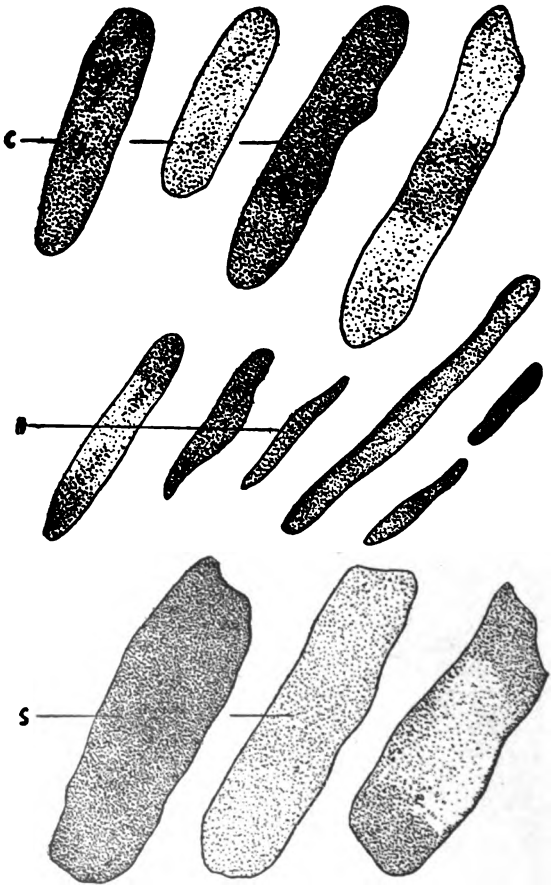
Blood Casts (× 500). (Heitzmann.) *C,* casts from convoluted tubules; *N,* from narrow tubules; *S,* from straight collecting tubules.

FIG. 69.



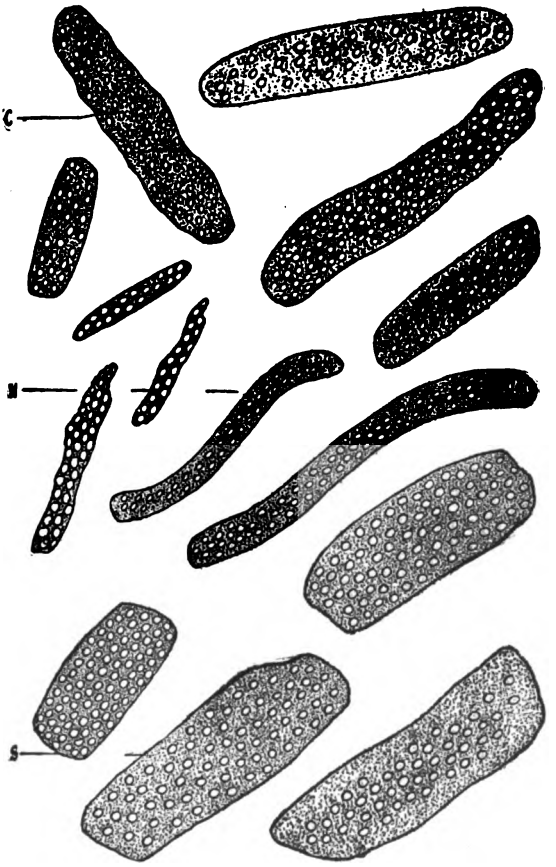
Epithelial Casts (× 500). (Heitzmann.) *C*, casts from convoluted tubules; *N*, from narrow tubules; *S*, from straight collecting tubules.

FIG. 70.



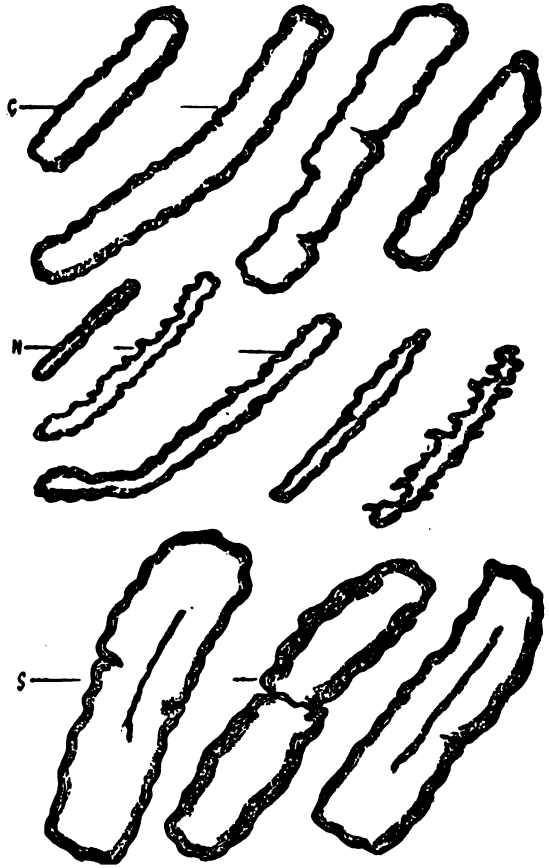
Granular Casts (× 500). (Heitzmann.) *C*, from convoluted tubules; *N*, narrow tubules; *S*, straight collecting tubules.

FIG. 71.



Fatty Casts (× 500). (Heitzmann.) *C*, from convoluted tubules; *N*, narrow tubules; *S*, straight collecting tubules.

FIG. 72.



Waxy Casts (× 500). (Heitzmann.) *C*, from convoluted tubules; *N*, narrow tubules; *S*, straight collecting tubules.

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